

# Silica gel functionalized with imidazolium group via click chemistry – new stationary phase for ion chromatography

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## Abstract

This manuscript describes the preparation of a simple effective ion-exchange material based on silica gel, on the surface of which methylimidazolium bromide is fixed using a click reaction. The resulting material was used as a stationary phase for the separation and determination of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ , and  $\text{SO}_4^{2-}$  using ion exchange chromatography. The separation efficiency and retention factors for the selected anions were studied in the pH range 3.5–6.5. The proposed material was used for the determination of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  in water and can be suggested for successful use in real water samples.

## Keywords

click reaction  
ion exchange  
modified silica

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## 1. Introduction

The development of new anion-exchange phases with improved efficiency and selectivity is one of the topical problems of modern ion chromatography [1]. The selectivity of an anion exchanger is largely governed by the nature and structure of functional layer and the method of its attachment to the matrix surface. The efficiency of an anion exchanger depends on the type of material, as well as on the morphology and the packing mode of particles. Organic polymers can be considered as the most convenient and common matrices for the design of anion exchangers. Nevertheless, such materials as zirconia, alumina, and, especially, silica gel are quite often used for the preparation of organomineral materials, stationary phases in chromatography and adsorbents for solid-phase extraction. The disadvantage of silica materials is their limited stability at lower and higher pH values, especially in alkaline solutions. Silica-based anion exchangers are often used in the pH range 2.0–9.5. However, compared to organic polymers, silica-based ion exchangers have the advantages of higher chromatographic efficiency and greater mechanical stability. In addition, such materials are preferable for operation in the nonsuppressive version of ion chromatography with conductometric detection, since in this case it is necessary to use dilute eluents, which is possible with materials of low exchange capacity.

Silica gel-based sorbents are synthesized using a conventional approach, which consists in the surface modifi-

cation with different functional groups. Functionalization through covalent attachment of a modifier to the matrix surface has a number of advantages. First, the required amount of sorption and ion-exchange centers is governed by the structure and amount of a modifier. Second, variation in the structure of a modifier can influence the capacity, efficiency, and separation selectivity of an ion. Third, there are cross linking agents which enable extending the working pH range to 9.2 without affecting the efficiency over the entire life cycle of a column [2].

Such surface-grafted anion exchangers have the advantage of a small thickness of the ion-exchange layer that favors an increase in the rate of mass transfer upon ion exchange and thereby makes it possible to separate ions with high performance and high selectivity [3].

Various classes of organic compounds are used as the surface modifiers of stationary phase matrices [4]. In recent years, there is a growing interest in the use of ionic liquids that enable a wide variation in the nature of a cationic moiety, which influences the properties of obtained materials [5–7].

Among ionic liquids, imidazolium salts gained widespread acceptance as modifiers. Examples of their use as efficient extractants capable of forming ion-associative complexes with simple and complex anions have been described. Such complexes are readily produced and quite stable and variation of functional groups in the cationic moiety of ionic liquids offer manifold possibilities to apply salts in different version of sample preparation:

sorption concentration, liquid-liquid microextraction, and modification of stationary phases in gas and liquid chromatography [7, 8].

Materials with attached imidazolium salts have been used successfully as stationary phases in liquid chromatography for separation of caffeine, theophylline, theobromine [9], xylose, glucose [10], ephedrine [11], and vitamins [12], as well as for separation of organic and inorganic anions [13–15]. Due to the variety of available starting reagents, not only materials for supernatant columns, but also solid columns with attached ionic liquids have been synthesized [16, 17].

The aim of the present work was to obtain ion-exchange materials based on silica gel having a particle size of 8–12  $\mu\text{m}$  with imidazolium salt covalently immobilized by click reaction and to study whether they can be used as a stationary phase for ion-exchange chromatography.

## 2. Experimental

### 2.1. Reagents and instrumentation

The sorbent was prepared using silica gel “Sorbfil” with a particle size of 8–12  $\mu\text{m}$ .

IR spectra were recorded on a Shimadzu IR Prestige spectrometer in a range of 400–4200  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR spectra were measured using a 400 MHz Bruker WB Avance III spectrometer operating at 9.39 Tesla equipped with a Bruker H-F/X 4 mm pencil CP/MAS probehead.  $^{13}\text{C}$  chemical shifts were referenced to external solid TSP ((trimethylsilyl)propionic acid sodium salt) standard. Cross-polarization technique from  $^1\text{H}$  with spinning sideband suppression (CP TOSS), contact pulse durations of 2–4 ms at a MAS rate of 10 kHz was used.

The thermal stabilities of modified silica gel samples were studied on an STA 409 PC Luxx synchronous thermal analyzer (Netzsch, Germany) in a temperature range from 30 to 1000  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  in the air atmosphere in  $\text{Al}_2\text{O}_3$  ceramic crucibles.

The pH value of working buffers was verified on an Expert-001 ionomer using a calibrated ESC-10608 combined glass electrode.

Chromatographic properties of the column packed with modified silica gel were studied using a modular high-performance liquid chromatograph from Shimadzu (Kyoto, Japan) including a CTO-20A column thermostat, an LC-20AD sp mobile phase feed module, and CDD-10A vp. conductometric detector. The volume of injection loop was 20  $\mu\text{l}$ . Data were collected and processed using the LCsolution program.

### 2.2. Column packing

316 Stainless steel HPLC columns (150 $\times$ 2 mm) (Phenomenex) were used. The chromatographic column was packed by the suspension method under a pressure of 13 MPa. A test portion of the modified silica gel was added to a  $\text{C}_2\text{H}_5\text{OH}-\text{CHCl}_3$  solution (1:1, v/v). The column was

packed and the sorbent was compacted on exposure to ultrasound. After packing, the column was conditioned by passing iso-propanol in a volume equal to the 20-fold volume of the packed column, next – bidistilled water, and then – a working mobile phase until the background signal has become constant.

### 2.3. Synthesis of imidazolium-modified silica gel

Acetonitrile (70 mL), 3-azidopropyl silica gel (5 g), 1-methyl-3-prop-2-yn-1-yl-1H-imidazolium (1 g), CuI (0.095 g), and N,N,N',N'-(tetramethylethylenediamine) (750  $\mu\text{L}$ ) were placed in a pressure flask with fluoroplastic screw cap and magnetic bar in the argon atmosphere. The resulting suspension was kept with vigorous stirring at 70  $^{\circ}\text{C}$  for 4 h. Silica gel was separated on a Schott filter, washed with acetone, water, 2 M hydrochloric acid, and again acetone and dried at 55  $^{\circ}\text{C}$  for 12 h under a residual pressure of 5 mm Hg.

A portion of the resulting modified silica gel was further treated with a solution of hexamethyldisilazane in toluene for 8 h at 80  $^{\circ}\text{C}$ .

### 2.4. Determination of the total exchange capacity of the modified silica gel

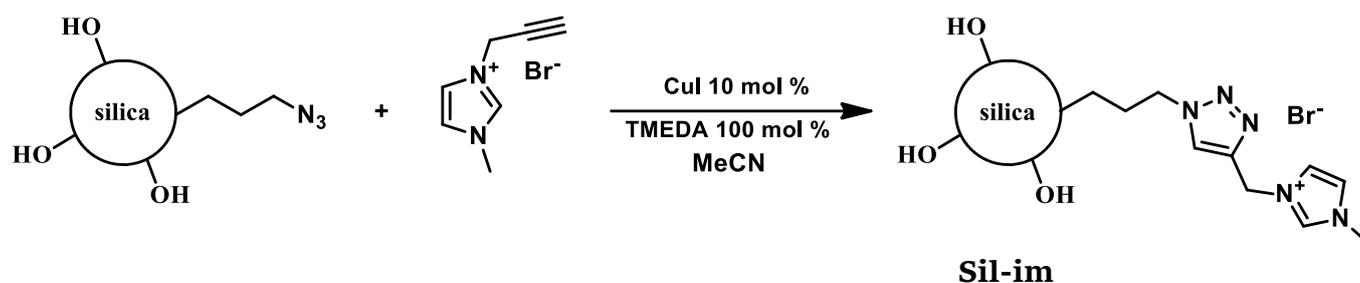
The maximum exchange capacity of the material was determined by titrimetry. The modified silica gel (0.5 g) was agitated with 0.1 M nitric acid (20 mL) for 1 h [18]. Silica gel was filtered off and the amount of chloride ion released after the ion exchange reaction with 0.1 M  $\text{HNO}_3$  was determined by titrimetry in an aliquot portion of the filtrate. To the aliquot portion of filtrate (5 mL), 0.05 M  $\text{AgNO}_3$  (5 mL) was added and the excess of unreacted  $\text{AgNO}_3$  was titrated with 0.05 M KSCN using a saturated solution of  $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2$  (0.2 mL) as an indicator. Titration was terminated after a sorrel color of the solution appeared due to the formation of iron rhodanate complex. The calculated total exchange capacity was  $0.26 \pm 0.02$  mM/g. The capacity of the silanized material remained unchanged.

## 3. Results and discussion

The test object was an organomineral material based on silica gel with a covalently attached imidazolium group obtained by the azide-alkyne cycloaddition click reaction (Scheme 1).

In  $^{13}\text{C}$  NMR spectrum for the modified silica gel with imidazolium salt two groups of spectral signals are seen. One group contains two signals at  $\delta$  124.4 and 137.4 corresponding to the carbon nuclei in nitrogen-containing ring. Another group consists of spectral signals at  $\delta$  52, 44.6, 36.8, 24.1, and 17, which corresponds to the carbon atoms of aliphatic  $-\text{CH}_2-$  fragments. The signal at  $\delta$  9.7 corresponds to the  $-\text{CH}_3$  group.

Fig. 1 shows the IR spectra for the starting silica gel with covalently attached azide group and the imidazolium-bearing material obtained according to Scheme 1.



**Scheme 1** Synthesis of the modified silica gel

Both spectra display a broad intense band at about 1300–1290  $\text{cm}^{-1}$  corresponding to stretching vibrations of the siloxane (Si–O–Si) bond in silica. The intense absorption band at 1627  $\text{cm}^{-1}$  is due to bending vibrations of water adsorbed on the silica gel surface. The broad intense band at 3200–3500  $\text{cm}^{-1}$  corresponds to the stretching vibrations of O–H adsorbed on the water surface and silanol groups. The intense absorption band at 2106  $\text{cm}^{-1}$  corresponds to stretching vibrations of the azido group grafted to the silica gel surface. In the spectrum of the silica gel sample obtained after the click reaction, the stretching vibration band of the azide group disappears, which suggests a successful click reaction on the silica gel surface.

The obtained batch of silica gel with a covalently immobilized group was divided into two portions. One portion was treated with a silanization reagent, hexamethyldisilazane (Scheme 2), in order to inactivate residual

silanol groups, which are additional sorption centers.

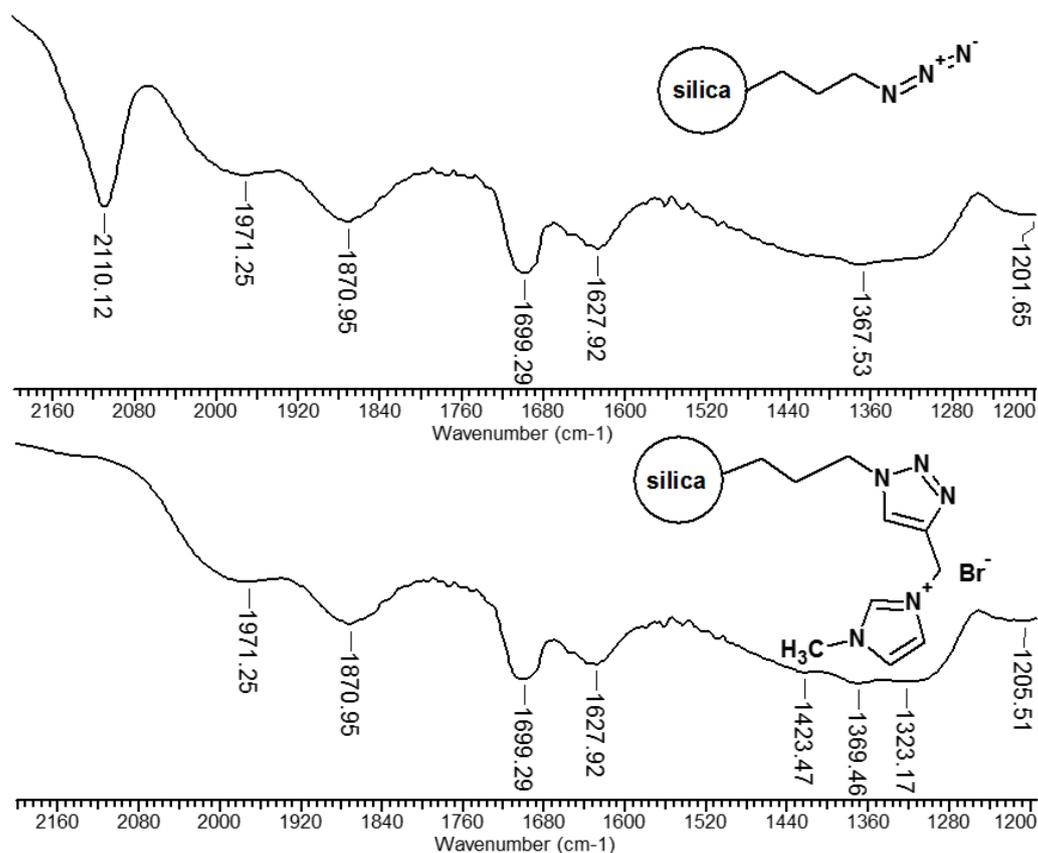
The second portion of the material was used without additional treatment.

The heat stability is one of the key characteristics of sorption materials, since it governs the temperature range of their possible application (Table 1).

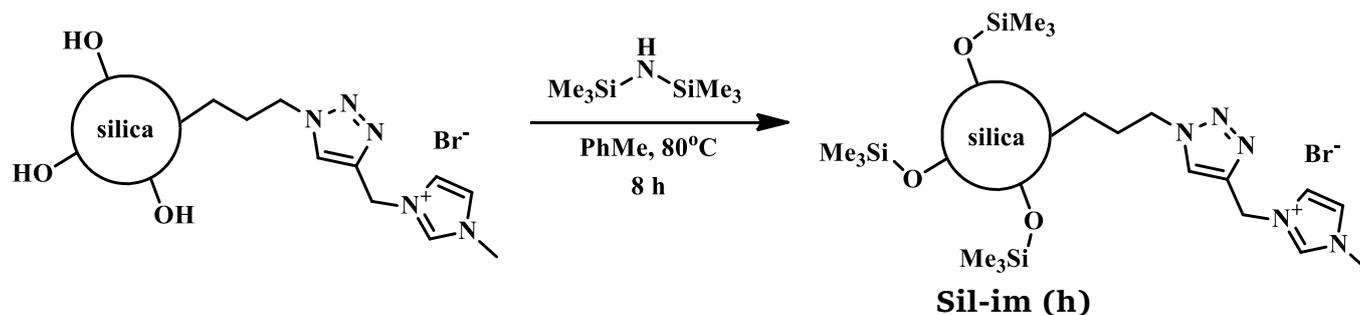
Similar temperature regions of weight loss and the presence of exothermic effect at about 350  $^{\circ}\text{C}$  can be distinguished for both samples of the modified silica gel.

**Table 1** Thermal analysis data of silica gel samples

Sil-im (h)		Sil-im	
Temperature range, $^{\circ}\text{C}$	Weight loss, %	Temperature range, $^{\circ}\text{C}$	Weight loss, %
30–154	4.7	30–165	2.8
154–85	6.1	165–325	4.4
285–566	10.7	325–460	3.6
566–950	0.2	460–900	4.1



**Fig. 1** IR spectra of the modified silica gel samples

**Scheme 2** Synthesis of the modified silica gel

According to the literature data [19], the first section on the TG curve in a range from 80 to 170 °C is due to the evaporation of water adsorbed on the silica gel surface. Further decrease in the sample weight in a range from 170 to 900 °C corresponds to destruction of the functional organic layer. The total weight loss of modified silica gel samples at 950 °C was about 16.0–21.7%.

Chromatographic conditions of the modified silica gels were studied in a single-column version of ion chromatography with non-suppressed conductivity detection. In such cases, for determination of anions on stationary phases possessing relatively low capacity values, diluted eluents based on aromatic acids, such as benzoic and phthalic acids, are preferred. The choice of the nature and composition of a buffer solution was caused by the fact that solutions based on phthalic acid possess high buffer capacity in the pH range recommended for stationary phases based on silica [20, 21].

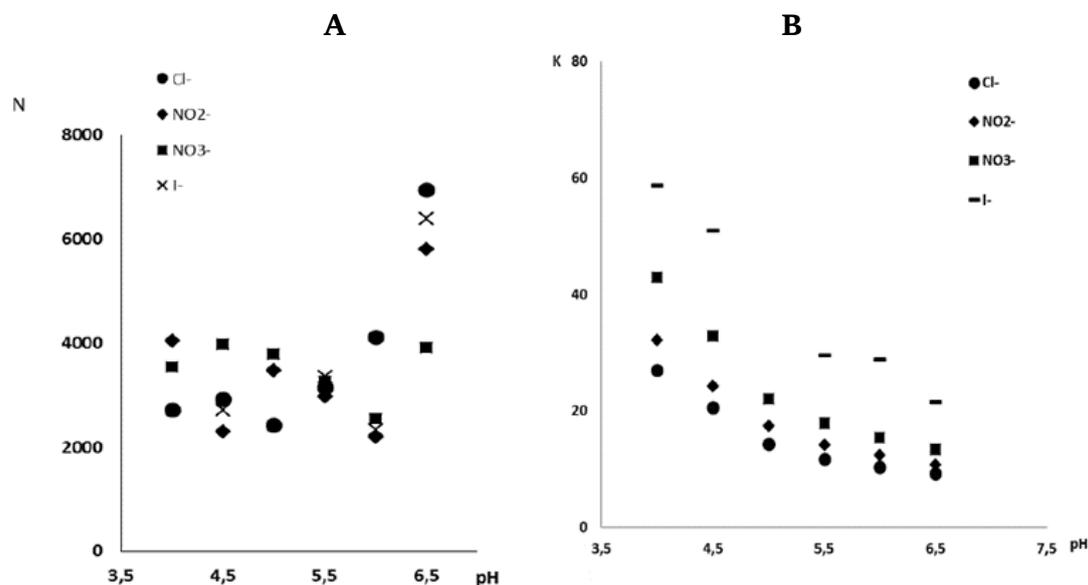
A mixture of  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ , and  $\text{SO}_4^{2-}$  anions was chosen as the model. The working parameters for chromatographic separation were chosen as follows: the eluent was  $\text{HOOC}_6\text{H}_4\text{COOK}$  with  $C = 2.5 \text{ mM}$  and  $\text{pH} = 4$  [22].

The comparison of the efficiency of separation of the standard anion mixture by the studied materials under identical conditions demonstrates a considerable decrease in the plate numbers per meter ( $N/m$ ) for Sil-im(h) (Table 2).

**Table 2** Efficiency of anion separation ( $N/m$ ) and retention time ( $t_r$ , min) on the Sil-im and Sil-im (h) sorbents

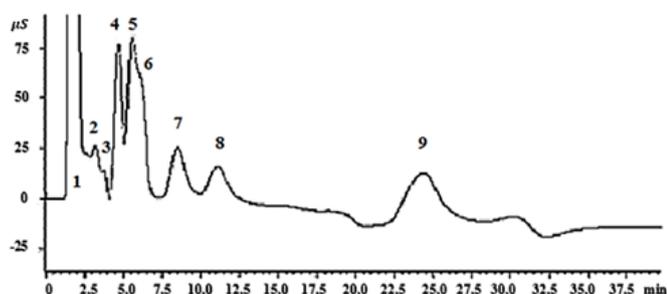
Anion	Sil-im		Sil-im (h)	
	$N$	$t_r$	$N$	$t_r$
$\text{Cl}^-$	3126	5.0	2720	11.8
$\text{NO}_2^-$	10093	5.9	4045	14.2
$\text{NO}_3^-$	8686	6.5	3546	17.8
$\text{I}^-$	6273	8.7	2808	29.6

The addition of NaOH to the stationary phase results in an increase in the efficiency and higher rapidity of separation of some anions due to an increase in the eluting power of the mobile phase. Upon pH change from 4 to 6, the concentration of hydrogen phthalate, an average-strength eluting ion, increases and, upon pH above 6, divalent phthalate with high eluting ability becomes the main anionic form of the eluent. In addition, at pH close to 7, the residual silanol groups on the surface of the anion exchanger, which can enter into ion exchange interactions, undergo almost complete ionization resulting in an increase in the separation efficiency (Fig. 2). The most efficient separation was observed at  $\text{pH} = 6.5$ ; one can note a multiple decrease in the retention, which leads to a possibility of determining anions in lower amounts. No change in the elution order was observed, which indirectly suggests a predominant ion-exchange mechanism of anion separation on the proposed stationary phase.

**Fig. 2** The effect of NaOH content in the mobile phase on the separation efficiency  $N$  ( $N/m$ ) (A) and the retention  $K$  of anions on the Sil-im(h) sorbent (B)

The linearity of the method was tested using a series of inorganic anions standard solutions. Each point of the calibration plot was the average of three peak height measurements, because the baseline resolution of some anions couldn't be achieved without further dilution of the mobile phase and significant decrease of efficiency, which could cause a problem in the analysis of the samples with complex matrices. An example of a typical chromatogram is shown in the Fig. 3. The coefficient for calibration curves, the linear range and detection limits (defined as a signal three times the height of the noise level) as well as the quantification limits are presented in Table 3.

The comparison of the quantitative characteristics by the example of univalent inorganic anions demonstrates narrowing of the working concentration range on going from Sil-im to Sil-im(h) and, as a consequence, an increase in the limit of detection of an analyte.



**Fig. 3** Chromatogram obtained with the Sil-im stationary phase using anion-exchange conditions. Test mixture: 1) F<sup>-</sup>; 2) CH<sub>3</sub>COO<sup>-</sup>; 3) IO<sub>3</sub><sup>-</sup>; 4) Cl<sup>-</sup>; 5) NO<sub>2</sub><sup>-</sup>+Br<sup>-</sup>; 6) NO<sub>3</sub><sup>-</sup>; 7) I<sup>-</sup>; 8) SCN<sup>-</sup>; 9) SO<sub>4</sub><sup>2-</sup>. Chromatographic conditions: mobile phase: 2.5 mmol/L HOCC<sub>6</sub>H<sub>4</sub>COOK with pH = 4, flow-rate: 0.3 ml/min, injection volume: 20 µl and detection: non-suppressed conductivity

**Table 3** Sensitivity factors and linear ranges of calibration curves for the studied anions

Anion	Sil-im(h)				Sil-im			
	Linear range, mg/L	a*	R <sup>2</sup>	LOD**, mg/L	Linear range, mg/L	a*	R <sup>2</sup>	LOD**, mg/L
Cl <sup>-</sup>	40-160	6227	0.9986	5.6	25-400	3494	0.9985	1.9
NO <sub>2</sub> <sup>-</sup>	20-160	2210	0.9983	4.9	25-400	2914	0.9990	1.6
NO <sub>3</sub> <sup>-</sup>	40-160	3859	0.9978	12.1	25-200	484	0.9982	3.8
I <sup>-</sup>	40-160	6325	0.9984	11.0	25-300	685	0.9925	11.2

\*a - coefficient for calibration curves ( $y = ax + b$ )

\*\*LOD limits of detection =  $S \cdot 3.3$ , S - standard deviation of ten independent measurements of a blank sample

**Table 4** Errors in the determination of the studied anions using the studied anion exchangers ( $n = 3, P = 0.95$ )

Anion	Sil-im(h)			Sil-im		
	Added, mg/L	Found, mg/L	Δ, %	Added, mg/L	Found, mg/L	Δ, %
Cl <sup>-</sup>	80	77.3±9.9	-3.4	100	94.5±14.1	-5.5
NO <sub>2</sub> <sup>-</sup>		78.3±10.2	-2.1		94.0±14.1	-6.0
NO <sub>3</sub> <sup>-</sup>		80.8±10.4	1.0		97.5±14.3	2.5
I <sup>-</sup>		81.5±10.6	1.9		106.2±16.2	6.2

**Table 5** Assessment of the anion content in the real sample using different chromatographic systems ( $n = 5, P = 0.95$ )

Stationary phase	Cl <sup>-</sup>			SO <sub>4</sub> <sup>2-</sup>		
	C, mg/L	C <sub>claimed</sub> , mg/L	S <sub>r</sub> , %	C, mg/L	C <sub>claimed</sub> , mg/L	S <sub>r</sub> , %
Sil-Im	2227±387	2200-7700	1.93	7321±425	5500-9000	0.17
Seporus A-UNI (HC-1)	2845±345		4.13	7691±880		3.87

However, the sensitivity of determination in this case increases, which is evidenced by an increase in the slope of the calibration curve. The error in the determination of standard solutions of the analyzed group of anions as estimated by the added-found method differs in a regular manner: no more than 6.2% for Sil-im and no more than 4% for Sil-im(h) (Table 4).

The applicability of the obtained ion-exchange material as a stationary phase in the ion-exchange chromatography was estimated by the example of Sil-im upon determination of inorganic anions in mineral water. Since the single-column non-suppressed ion chromatography used in this study does not possess a high sensitivity compared to two-column with suppressed conductivity detection, although it allows one to determine simultaneously in the isocratic mode weakly and strongly retained anions, it seems interesting to analyze real objects with a high content of anions. A "Lyso-gorskaya" bottled mineral drinking water relating to a group of chloride-sulfate ones was chosen as the test object (Table 5). The content of main macrocomponents was estimated by the calibration curve. To verify the determination accuracy of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, their contents in the sample were estimated using a commercial column on a DIONEX ICS-300 chromatographic system with a possibility of eluent generation and suppressed conductivity detection.

The confidence intervals of ion determination obtained for different chromatographic determination systems overlap, which suggests the accuracy of the obtained data.

## 4. Conclusions

In this work, the possibility of modifying the silica gel surface with an imidazolium salt using a click reaction was shown. The resulting ion exchange material was used as a stationary phase in the ion exchange chromatography method to separate  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ , and  $\text{SO}_4^{2-}$ . The study showed that the proposed material allows the determination of the selected anions with an error of 3.5–6.0%. Moreover, the developed material showed good stability and repeatability of the results of the determination and separation of anions during the operation.

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## Conflicts of Interests

The authors declare that they have no competing interests.

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