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Physicochemical properties of silica gel coated with a thin layer of polyaniline (PANI) and its application in non-suppressed ion chromatography

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ABSTRACT

Physicochemical properties of a new sorbent and its potential application in non-suppressed ion chromatography (IC) have been investigated. The sorbent was obtained in a process of covering silica gel particles with a film of polyaniline (PANI).

The properties of silica modified with polyaniline such as particle size, porosity, average quantity of polyaniline covering carrier and density of sorbent were determined. In our study the following methods were used: microscopic analysis, laser diffraction technique, combustion analysis, mercury porosimetry and helium pycnometry. Column with the newly obtained packing was used for the separation of inorganic anions. Optimized chromatographic system was successfully employed for analysis of iodide and bromide in selected pharmaceutical products (Bochnia salt and Iwonicz salt) applied in chronic respiratory disease. Analysis was carried out using 0.1 M solution of HCl in mixture of methanol/water (50:50 v/v) as a mobile phase; the flow rate was 0.3 mL min^{-1}, temperature was 24 °C and $\lambda = 210$ nm. Validation parameters such as correlation coefficient, RSD values, recovery, detection and quantification limits were found to be satisfactory.

1. Introduction

Ion chromatography (IC) is the main and the most popular method for determining of anions in samples with various matrices [1,2]. Different types of support materials have been applied in IC technique including silica gel and alumina [3]; however, recently organic polymer based stationary phases have the greatest importance because of their stability in extreme pH values [4,5]. The most common commercially available columns are based on resin or latex ion exchangers and are dedicated for suppressed ion chromatography.

On the other hands, non-suppressed ion chromatography (single column IC) is also a useful and alternative technique for anions analysis. Its main advantage is lower cost of equipment because suppressor and eluent generator are not required, thus standard HPLC system can be used for ion analysis [6–8]. There are some literature data about developing and synthesis of stationary phases for non-suppressed IC. Silica is usually used as support material for different modifications, e.g., phenyl–aminopropyl [9,10], vitamin U [7], imidazole [11,12], pyridine [13,14] and benzimidazole [15]. Covering the surface of silica improves its stability toward extreme pH value [16,17].

Polyaniline (PANI), which is typically obtained by the oxidation of aniline or anilinium salts, is one of the most important conducting polymers [18–22]. Its commercial applications are a subject of interest for many researchers because of its interesting unique physical and chemical properties such as: good conductivity, stability, easy preparation, affordability and redox properties in comparison to other conducting polymers [23]. PANI has been applied in diverse areas including chemistry, physics, optics, materials and biomedical science [24,25], however, its use in a separation technique is not a common practice and focus mainly on solid phase extraction (SPE) [26,27].

The aim of our work was investigation of the physicochemical parameters of a new stationary phase based on silica covered with polyaniline and optimization chromatographic conditions for separation of inorganic anions. The following properties were determined: amounts of polyaniline (PANI) deposited on the surface of silica gel, as well as particle size, the porosity and density of the obtained sorbent. The potential application of synthetized stationary phase for

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determination of iodide by non-suppressed IC was also investigated. This anion is essential microelement and its quantification, especially in samples with high matrix of chloride is difficult. Moreover, limit of detection values (LOD) obtained for suppressed IC are unsatisfactory, thus the development of new stationary phases for iodide analysis it seems to be still important analytical task [7,8,28].

2. Material and methods

2.1. Reagents and solutions

Reagents: ammonium persulphate, acetonitrile, chloroform, methanol and standards of anions were of analytical grade from Merck (Darmstadt, Germany). Water was redistilled and deionised by use of EasyPure RF system (Bearnsted, USA). The resistance of water was 18 MΩ cm^{-1}. Silica gel LiChrosorb Si 60 (irregular shape, surface area 490 $m^2\ g^{-1}$) and LiChrospher Si 60 (spherical shape, surface area 650 $m^2\ g^{-1}$), particle size 10 μm (Merck, Darmstadt, Germany) was used as support for the stationary phase. Aniline (POCh, Gliwice, Poland) was purified by distillation under the partial vacuum on the QuickFit apparatus (Great Britain).

2.2. Preparation of silica covered with polyaniline film

30.0 g of the deaerated silica gel was placed in a 500 mL flask, mixed with 200 mL of 0.2 M aniline hydrochloride solution and 50 mL of 1 M hydrochloric acid solution and immersed in ice bath. Slow addition of ammonium persulphate solution was started, when the temperature reached 2 °C. The temperature of the reactionary mixture should not exceed 4 °C (the reaction is exothermic), otherwise the low-weigh oligomers of aniline were formed [29].

Short-chain oligomers of aniline are soluble in acetonitrile, chloroform and methanol, therefore the obtained sorbent was washed several times with small portions of these solvents.

2.3. Physicochemical studies

Silica gel coated polyaniline and silica gel (as a reference) were dried at 105 °C to constant weight. 3.0 g of adsorbent sample was applied to each analysis. All experiments were performed at room temperature (20 ± 1 °C).

2.3.1. Microscopic analysis

Microscopic analysis was performed in order to observe any changes occurring during the polymerization process. The samples were observed in optical microscope (PZO, Poland).

2.3.2. Particle size distribution analysis

Particle size analysis was conducted using a laser particle size analyzer Mastersizer 2000 (Malvern Instruments, Great Britain). The samples representing both types of silica gel were suspended in deionized water and dispersed by a magnetic stirrer; dispersion was additionally assisted by ultrasounds for 4 min. The obtained suspension was automatically sampled and analyzed.

2.3.3. Combustion analysis

Combustion analysis was performed to determine the amount of polyaniline coating of silica gel. 1 g of silica and silica covered with polyaniline were placed in a combustion furnace at 700 °C for 4 h. After cooling, the samples were accurately weighed and amount of PANI was calculated based on the weight difference.

2.3.4. Porosimetry analysis

Porosimetry analysis was performed on a mercury porosimeter Autopore IV 9500 (Micrometrics, USA), with measurement ranger for pore radius amounting from 0.003 μm to 360 μm at maximum pressure 33,000 psi. The samples were degassed in vacuum, immersed in mercury and then mercury was pressed into the porous structure of investigated sorbent under stringently controlled pressure variations.

2.3.5. Helium pycnometry

The investigations of density of silica and silica modified with polyaniline samples were performed by Ultrapycnometer 1000 (Quantachrome, USA). The samples were placed in a measurement cell and analyzed using helium as the displacing fluid. Helium is recommended, because its small atomic dimension enables entry into pores approaching 0.2 nm.

2.4. Chromatographic analysis

Adsorbent was suspended in mixture of methanol–dioxane–carbon tetrachloride (10:45:45) and next packed in stainless steel HPLC columns of 250 mm length and the internal diameter of 2.1 mm at a maximum pressure of 600 bar using a compressed gas-driven slurry packer.

The Dionex model DX-500 ion chromatograph (Sunnyvale, USA), equipped with a 25 μL sample loop, an IP25 isocratic pump and an UV spectrophotometric detector ($\lambda=210$ nm) was used in the analysis of selected anions. As eluent, mixture of 0.1 M methanolic HCl and 0.1 M aqueous HCl (50:50, v/v) was used. The flow rate was 0.3 mL min^{-1}, temperature was 20 °C.

2.4.1. Sample and standard preparation

Stock solutions of investigated ions were prepared in deionized water (18.2 MΩ cm^{-1}). Standard solutions were prepared by dilution of stock solutions. 0.5102 g Bochnia salt (Salco, Poland) and 0.5054 g. Iwonicz salt (Spa Iwonicz Poland) was dissolved in deionized water and made up to 100 mL.

3. Results and discussion

3.1. Microscopic analysis

Conditions and reagents used during the synthesis of new stationary phases may cause destruction of the carrier particles. Therefore, the obtained sorbent was initially assessed using an optical microscope. It could be stated that the grains of silica gel were not crushed during the process of synthesis. Lack of low-weight molecules of polyaniline was also noted, which proves the efficiency of purification process. Blue coloration of the surface of silica gel observed shows that the gel surface was covered by polyaniline (Fig. 1).

3.1.1. Particle size distribution analysis (laser diffraction method)

A laser diffraction particle size analysis is based on laser light scattering measurement by the particles of stationary phase suspended in a liquid. This method allows determining the homogeneity on particle size distribution of the samples.

On a curve illustrating the particle size distribution of silica gel the main maximum is situated near 9.9 μm (Fig. 2). The second curve obtained for modified silica is slightly shifted (about 1.6–2.3 μm) in the direction of higher values, which is presumably associated with the presence of PANI film deposited on silica. It is also noticed the absence of small-sized particles which indicates an effective purification PANI sorbent both from the crushed grains of gel and low molecular products of synthesis of polyaniline. The presence of

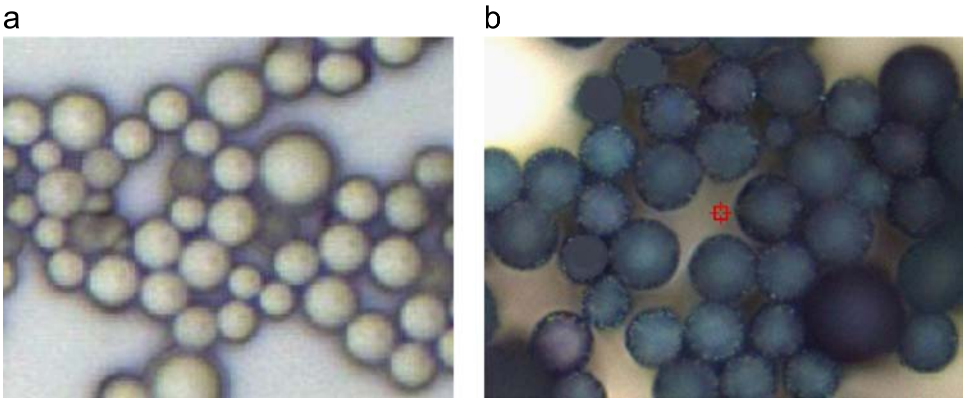

Fig. 1. Optical microscope picture of: (a) LiChrospher silica; and (b) LiChrospher silica covered with polyaniline.

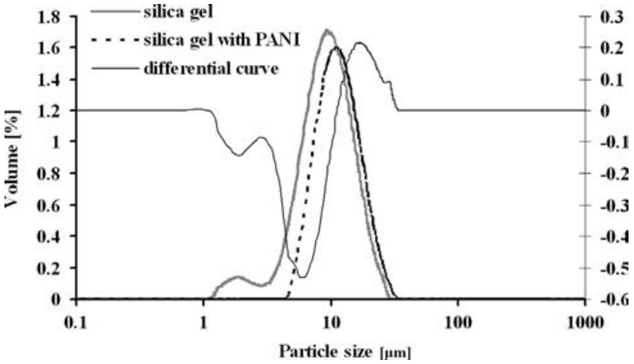

Fig. 2. Particle size distribution of silica gel and silica gel with polyaniline obtained using the laser diffraction method.

Table 1
Parameters of particles size arrangement of silica gel and silica modified with polyaniline.

Parameter	Silica gel	Silica gel with PANI
Average diameter of grains in μm	9.982	12.287
Lower decile, *d*(0.1) in μm	6.4	7.961
Median, *d*(0.5) in μm	11.474	13.28
Upper decile, *d*(0.9) in μm	19.394	21.816

small-sized particles is undesirable and may be the cause of increasing flow resistance and pressure in the chromatographic system. Changes of particle size during the deposition of PANI on silica gel are more visible on the curve differential. Table 1 presents the parameters of particle size distribution of both types of analyzed sorbents.

3.1.2. Combustion analysis

Amount of PANI deposited on adsorbent surface was calculated from the difference of weight of the samples of silica and silica modified with polyaniline, obtained from the combustion analysis. Average quantity of polyaniline covering carrier amounted the 5.39% ($n=5$). It constitutes 39% amounts of substrates used in synthesis. Significant part of low-weight polyaniline was removed during the purification process.

3.1.3. Porosimetry analysis

The mercury porosimetry analysis allows the calculation of parameters such as: pore size distribution of the sample, the total pore volume, the total pore surface area, average pore diameter [30–32]. This technique can provide useful information relating to the pore shape, network effects and skeletal and bulk density [33]. These parameters are particularly important because they influence the sorption properties of stationary phase and hydraulic permeability of mobile phase in chromatography.

The pressure required to press mercury into the porous structure is a function of pores radius, according to Washburn's equation.

$$P = 2\lambda_{Hg} \cos\,\theta / r$$

where: P—external pressure used in a vacuum chamber, λ_{Hg}—surface tension of mercury at 20 °C ($480\ \mathrm{mN\,m^{-1}}$), θ—angle of wetting with mercury of studied material, and r—radius of pores.

The pores size was determined assuming commonly cylindrical shape of pores. The experimental data obtained from the porosimetry analysis is shown in Fig. 3.

Two significant changes in the volume of pressed mercury, visible on the two curves indicated the presence of pores in the range: 1–2.5 μm and 0.002–0.003 μm which corresponds to pores between the grains and pores inside grains, respectively. Based on the differential curve, slight reduction of diameters of the pores inside the grain of silica gel with polyaniline was observed, while the spaces between the grain have increased in comparison with initial silica gel. The reason is deposition of a layer of polyaniline on their surface.

Some basic parameters obtained based on the porosimetry analysis of the investigated samples are given in Table 2.

3.1.4. Helium pycnometry

Density measurement of analyzed material by helium pycnometry is based on a measurement of a volume of a weighed sample. The density calculated based on volume of the investigated samples reached the value of 2.9928 ($\mathrm{g\,mL^{-1}}$) for silica gel and 2.4010 ($\mathrm{g\,mL^{-1}}$) for silica modified with polyaniline. Density of silica coated polyaniline was reduced by 19.77% in comparison with non-modified silica. This fact can be explained by low density of polyaniline ($1.22\ \mathrm{g\,mL^{-1}}$).

3.2. Optimization of chromatographic parameters

The obtained sorbent was used to fill a chromatography column (2.1 mm × 250 mm) in order to its testing as the stationary phase in ion chromatography. Iodate (V), nitrate (V), bromide, and iodide were chosen for experiments. Special attention was paid for iodide anion because of their biological importance and difficulty in trace analysis caused the high concentration of chloride matrix in environmental and pharmaceutical samples [7,28,34]. Conductivity detection is preferred for anion analysis however obtained LOD value for iodide

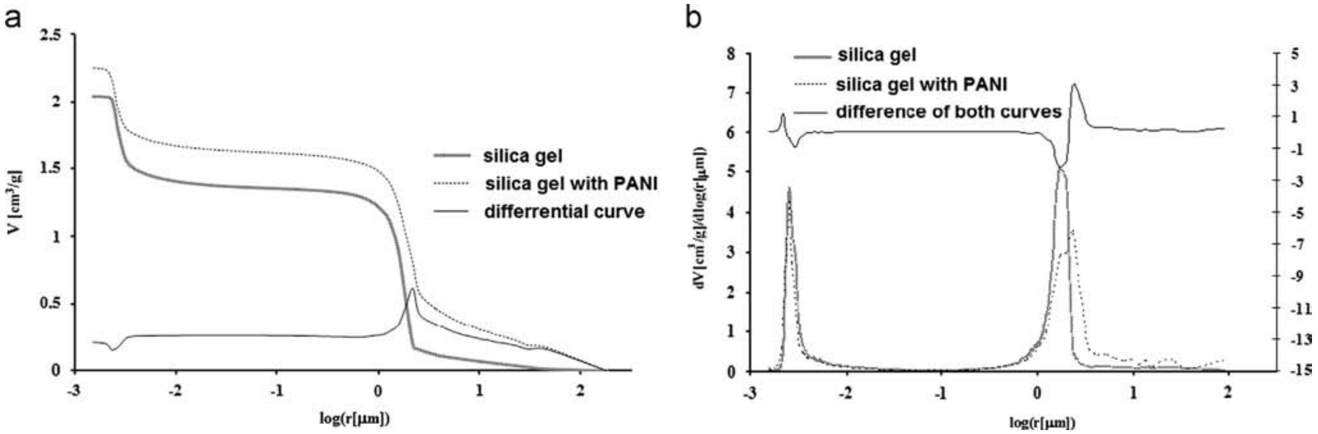

Fig. 3. Cumulative (a) and differential (b) distribution curves of silica gel and silica gel with polyaniline obtained using mercury porosimetry analysis.

Table 2
Selected parameters of analyzed samples obtained with use mercury porosimetry.

Sample	Total volume of pores (mL g^{-1})	Total area (m^2 g^{-1})	Median pore diameter (area) (nm)	Skeletal density (g mL^{-1})	Bulk density (0.0036 MPa) (g mL^{-1})	Porosity (%)
Silica gel	2.044	445.27	5.4	1.871	0.388	79.27
Silica gel with PANI	2.253	425.89	5.1	1.568	0.346	77.93

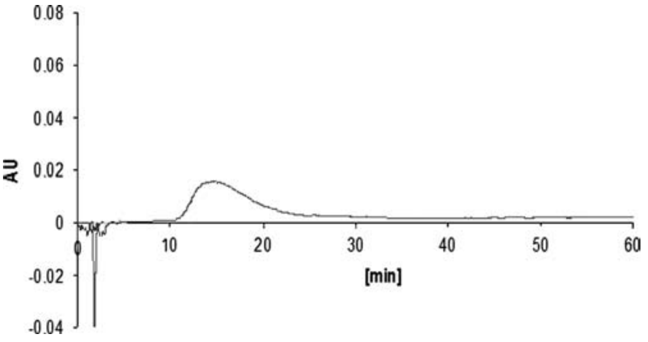

Fig. 4. Analysis of iodide with use of aqueous solution $Na_2CO_3/NaHCO_3$ (3.5 mM/1 mM).

Table 3
Chromatographic parameters such as retention factor values and theoretical plates for investigated anion.

Anion	$Na_2CO_3/NaHCO_3$		HCl/water		HCl in methanol/water	
	k	*N*	*k*	*N*	*k*	*N*
Iodate	0.99	201	1.31	1246	1.49	2254
Nitrate	2.32	154	1.97	1332	2.09	2656
Bromide	6.65	185	2.95	2653	3.15	3645
Iodide	7.32	60	4.70	1004	5.52	2254

Methanol was the marker to calculate t_0.

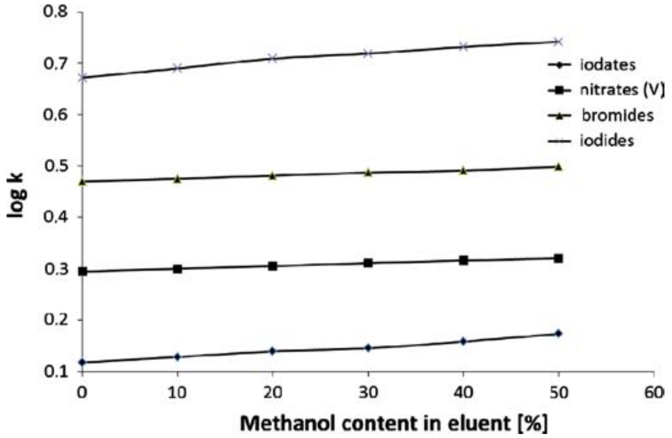

Fig. 5. Relationship between organic modifier concentration and log values of retention factor (*k*) for iodates (*V*), nitrates (*V*), bromides and iodides. Chromatographic condition: mobile phase 0.1 M HCl in mixture of water: methanol, flow rate 0.3 mL min^{-1}.

Table 4
Comparison of chromatographic parameters for investigated anions obtained on LiChrosorb with PANI and LiChrospher with PANI as a stationary phases.

Anion	LiChrosorb with PANI				LiChrospher with PANI			
	A	*N*	*α*	R_S	*A*	*N*	*α*	R_S
Iodate	1.13	2254	–	–	1.20	3018	–	–
Nitrate	1.10	2656	1.40	2.49	1.09	3887	1.78	4.49
Bromide	1.11	3645	1.51	3.87	1.04	4868	1.86	6.30
Iodide	1.49	2254	1.75	4.31	1.29	3061	1.94	5.67

A—asymmetry of peak; *N*—number of theoretical plates; *α*—separation factor; R_S—resolution factor.

in this technique are insufficient (about 0.1 ppm) thus spectrophotometric, potentiometric or amperometric detection is recommended for their trace determination [35–37]. In our investigations, UV–vis detector was employed for the simultaneous analysis iodide and the other ions in single chromatographic run.

The elution was performed in isocratic mode. The composition of eluents was chosen experimentally.

Frequently used in anion analysis alkaline eluents e.g. aqueous solution of NaOH or KOH (0.1 mM) possessed too high elution strength and the investigated anions were not retained on stationary phase. On the other hand, mobile phase containing aqueous solution of $Na_2CO_3/NaHCO_3$ in different proportions caused broadening and tailing of peaks (Fig. 4).

During the working with alkaline solution, eluate was checked colorimetrically using the silicomolybdate complex method. On the basis of obtained results we could state that silica was not dissolved by used mobile phases.

It was noticed that retention strongly depends on pH of eluents; thus acidic aqueous mobile phases containing HCl, H_2SO_4 or H_3PO_4, with various concentrations were further investigated. The best separation and shape of peaks was obtained for 0.1 M solution of HCl.

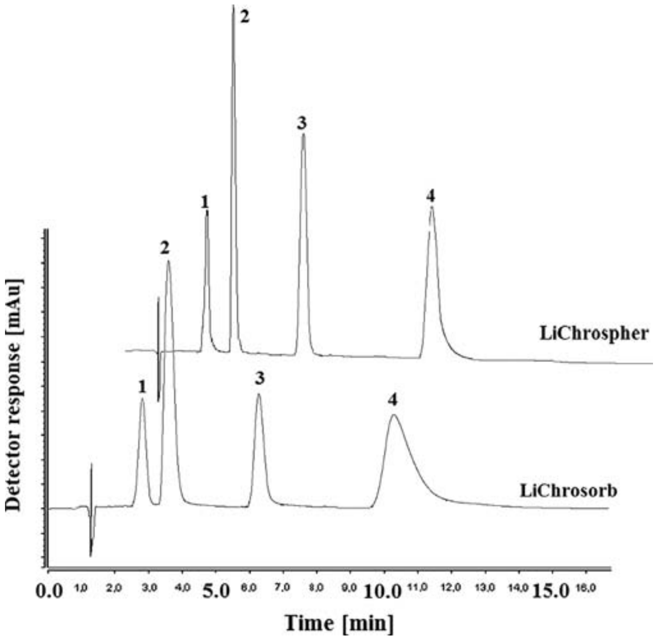

Fig. 6. The separation of: 1-iodate (*V*), 2-nitrate (*V*), 3-bromide and 4-iodide on LiChrosorb with polyaniline and LiChrospher with polyaniline. Chromatographic condition: mobile phase 0.1 M HCl in mixture of water: methanol (50:50), flow rate 0.3 mL min^{-1}, temperature 20 °C and λ=210 nm.

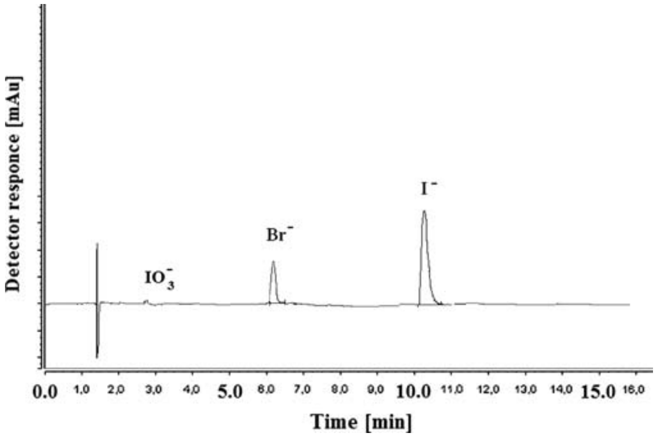

Fig. 7. The example of analysis of pharmaceutical product ("Salt Iwonicka") with use of LiChrospher with polyaniline. Chromatographic conditions are the same as in Fig. 6.

It was also observed that addition of organic modifier influenced the efficiency of the chromatographic system. Selected chromatographic parameters for various eluents are presented on Table 3. Relationship between organic modifier concentration and log values of retention factor (k) is presented in Fig. 5. In next part of our investigations we try to improve the efficiency of the chromatographic system by use of spherical silica for preparing the PANI coated stationary phase. As can be seen in Table 4, number of chromatographic plates increased and the shape of peaks were improved.

The example of chromatograms of investigated anions obtained on angular and spherical silica-PANI adsorbent is presented in Fig. 6.

3.2.1. *Sample analysis*

Iodide and bromide are essential micronutrient occurring in food, water and pharmaceutics. Thus, the optimized chromatographic system was used in the analysis of those anions in selected pharmaceutical products with large amount of chloride: Bochnia salt and Iwonicz salt, which are applied in chronic respiratory disease. Iodide and bromide have anti-inflammatory and antiseptic effect, on the other hand their large amount can have negative influence the human health. Excess of iodine can cause hypothyroidism as well as hyperthyroidism [38]. Bromide, iodide and small amount of iodate (*V*) were detected in both tested preparations (Fig. 7). The basic validation parameters: concentrations range, linearity, correlation equations, limit of detection and quantification are presented in Table 5. The obtained results for quantification analysis are summarized in Table 6. The concentration of iodate (*V*) was below limit of quantification.

Proposed system enables chromatographic analysis of selected anions using standard UV–vis HPLC instead of HPIC equipped with a suppressor and conductivity detector. Limits of detection for investigated anions are comparable to literature data [8,35,39] and the tested stationary phases can be prepared relatively simple and at low costs.

As shown in our earlier investigation [27] the advantage of silica gel covered with polyaniline film is highly chemically resistant to drastic inorganic and organic reagents and possibility working in a wide pH range.

Table 6
The results of quantitative analysis of pharmaceutical products.

Anion	t_r min ± SD (n=10)	Average content mg g^{-1} (n=10)	SD	% RSD	% Recovery
Bochnia salt, "Salco" Poland					
Bromide	6.70 ± 0.05	0.5014 mg g^{-1}	0.0074	1.48	98.2
Iodide	11.01 ± 0.09	0.3002 mg g^{-1}	0.0060	2.01	97.9
Iwonicz salt, "Spa Iwonicz" Poland					
Bromide	6.68 ± 0.06	1.2018 mg g^{-1}	0.0201	1.67	98.4
Iodide	11.03 ± 0.10	0.3331 mg g^{-1}	0.0063	1.89	97.7

Table 5
The basic validation parameters for analyzed anions.

Anion	Concentration range (mg L^{-1})	Correlation equation	Correlation coefficient	LOD (mg L^{-1})	LOQ (mg L^{-1})
Iodate	0.018–0.5	y=0.0057x+0.0046	0.9897	0.006	0.018
	0.018–10	y=0.0049x+0.0038	0.9941		
Bromide	0.029–0.5	y=0.0081x+0.0065	0.9971	0.012	0.029
	0.029–10	y=0.0051x+0.00005	0.9985		
Iodide	0.012–0.5	y=0.0066x+0.0041	0.9965	0.004	0.012
	0.012–10	y=0.0037x+0.00033	0.9989		

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