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O. Stashkiv^a, *V. Vasylechko*^{a,b}, *G. Gryshchouk*^a**SORPTION OF GADOLINIUM ON ACID-MODIFIED CLINOPTILOLITE**^a **Ivan Franko National University of Lviv, Lviv, Ukraine**^b **Lviv University of Trade and Economics, Lviv, Ukraine**

The sorptive properties of the acid-modified Transcarpathian clinoptilolite towards Gd(III) under dynamic conditions were investigated. The sorption capacity of the clinoptilolite in H-form depends on the nature and concentration of acid-modifier. The most effective sorption of Gd(III) was observed when clinoptilolite was pretreated with 1 M H₂SO₄ solution. The sorption capacity of the H-form of Transcarpathian clinoptilolite towards Gd(III) significantly depends on the concentration of gadolinium salt, the pH of solution and the temperature of the preliminary calcination of the sorbent. The sorption capacity of H-clinoptilolite under optimal conditions (diameter of zeolite grains was 0.20–0.31 mm; flow rate of gadolinium(III) solution with concentration 0.5 µg/mL through sorbent was 5 mL/min; and pH 10.0) was 8.2 mg gadolinium per 1 g of acid-modified clinoptilolite. The H-clinoptilolite sorbs the Gd(III) trace amounts even in the presence of other common ions. The solutions of 1 M HCl and 1 M KCl acidified by a hydrochloric acid to pH 4.0 are the most effective desorbents of gadolinium(III) ions from H-clinoptilolite. The method for gadolinium trace amounts preconcentration from aqueous solutions in a solid phase extraction mode with a further determination of this rare earth element by a spectrophotometric method was developed. The detection limit of this method is 0.3 ng/mL, and the linearity was evaluated in the range of 1–200 ng/mL.

Keywords: gadolinium, sorption, preconcentration, H-clinoptilolite, solid phase extraction.**DOI:** 10.32434/0321-4095-2019-127-6-197-204**Introduction**

Rare earth elements (REEs) and their compounds are widely used in industries as lasers, alloys, phosphors, rechargeable hydride batteries, permanent magnets, catalytic converters and glasses. Some REEs are also used as anticancer agents. Gadolinium is one of the most widely spread elements from the yttrium subgroup of lanthanides. This element finds various applications in electronics, optical ceramics, nuclear power and cryogenic technology, as well as component of luminescent materials, magnets and data storage media. The gadolinium compounds can be used as the reagents in magnetic resonance imaging.

The application of gadolinium in industry increases and that is why more and more quantities of this metal leak into the environment. Therefore, it is necessary to develop new sensitive, selective and precise methods of Gd determination in different environmental matrices including water. It is difficult to determine REEs directly due to very small

quantities of these elements in environmental samples. Moreover, the composition of a matrix affects the determination of rare earth ions. The preliminary preconcentration and separation of REEs from environmental objects and technological solutions must be performed in order to obtain precise and reliable results. One of the most widely used sample pretreatment techniques in the analysis of REEs is a solid phase extraction (SPE). This method has numerous advantages in comparison with other preconcentration methods, for example: simple operation, high preconcentration factor, rapid phase separation and ability to be combined with different techniques. Various substances such as modified silica gel [1], magnetic nanoparticles [2] and highly dispersive multi-walled carbon nanotubes [3] have been earlier used as solid phase sorbents of Gd.

Zeolites have found a variety of applications in catalysis, adsorption, agriculture, electronics and medical diagnostics due to the unique porous properties [4]. Natural and synthetic zeolites are used

as sorbents in SPE [5]. Natural zeolites show high adsorption ability at low concentrations of sorbed substances compared to many other natural aluminosilicates. Clinoptilolite is the most widely spread natural zeolite. It is often used as sorbent in the solid phase extraction methods and in sorption-luminescent methods for the determination of inorganic and organic substances microquantities [6–12,15]. This zeolite is characterized by stability to aggressive medium, mechanical strength, high sorption capacity and selectivity, ability of modification and regeneration, thermal stability, low cost and accessibility. Transcarpathian clinoptilolite, in contrast to common ion exchangers, has a sieve effect along with ion-exchange properties. This provides great opportunities for the development of selective methods for preconcentrating, separating and removing various substances.

One of the methods of natural zeolites activation is their treatment with an acid. The sorption properties of acid-modified clinoptilolite are significantly different as compared with such properties of the natural one. Transcarpathian clinoptilolite is highly siliconized and stable against acids, therefore its H-form can be obtained by the treatment with an acid. Previously, we have investigated the sorption properties of the natural form of Transcarpathian clinoptilolite towards Gd(III) [8].

The subject of the present work is the investigation of the influence of various factors (the nature and concentration of an acid-modifier, pH, preliminary thermal treatment of sorbent, concentration of Gd(III) and the type of buffer solution) on the Gd(III) sorption on the acid-modified Transcarpathian clinoptilolite and the evaluation of the possibility of the application of this sorbent in the solid phase extraction.

Experimental

The clinoptilolite used in this investigation was obtained from the deposit near the village Sokyrnytsia in the Ukrainian Transcarpathian region. Analysis showed that the main component is present within the range of 85–90%. The specific surface area of this clinoptilolite, determined by water sorption, is 59 m²/g. The clinoptilolite formula expressed in the oxide form (mass fraction) is as follows: SiO₂ 67.29; Al₂O₃ 12.32; TiO₂ 0.26; Fe₂O₃ 1.26; FeO 0.25; MgO 0.99; CaO 3.01; Na₂O 0.66; K₂O 2.76; and H₂O, 10.90. The zeolite samples were grained in a ball-mill, the grain fraction with the size of 0.20–0.31 mm was selected, washed with distilled water and dried at room temperature.

The method for the preparation of the acid-

modified clinoptilolite was as follows. The grained sample of zeolite (6 g) was pre-treated with 200 mL of 1 M H₂SO₄ for 24 h at the temperature of 20±1°C. After separation from acid solution, the sorbent was washed properly in distilled water. The clinoptilolite H-form was dried at room temperature. The thermal treatment of H-clinoptilolite was performed at required temperature in the oven for 2.5 h.

All used reagents were analytical grade. Standard aqueous solutions of gadolinium nitrate (with the concentration of 1.0 mg/mL) were prepared by dissolving the metallic gadolinium (99.9% purity) in the nitric acid solution (1:1). The working solutions of Gd(III) were prepared by the appropriate dilution of the standard solution. The 0.05% solution of sulfarsazene was prepared using 0.05 M Na₂B₄O₇ aqueous solution; bidistillate was used for all other reagent solutions.

The adsorption properties of acid-modified clinoptilolite were studied under dynamic conditions in a SPE mode. A sorption cartridge which consists of quartz tube (7 mm in diameter and 20 mm in length) filled with acid-modified clinoptilolite was used. The tube was closely retained in poly(vinyl chloride) frame which allowed the passage of solution in and out of the acid-modified sample. The solution of Gd(III) salt was passed through a cartridge for preconcentration filled with 0.6 g of the sorbent at 5 mL/min flow rate using a peristaltic pump. The passage moment of Gd(III) ions was fixed by the photometric method using the reaction of Gd(III) with sulfarsazene. It is a highly sensitive method of Gd(III) determination (LDL=100 ng/mL). This gave opportunity to determine the passage point of Gd(III) using DR/4000 V spectrophotometer (HACH) at a wavelength of 540 nm.

In order to recover the sorbed Gd(III) ions from the zeolite bed, 15 mL of eluent were passed through the sorption cartridge at the flow rate of 0.5 mL/min. The eluates were collected in the volumetric flasks of 25 mL and the volume was adjusted to the mark by adding double distilled water. Since solutions of mineral acids and pre-acidified solutions of alkali metals are efficient desorbents of Gd(III) from H-clinoptilolite, the solutions received after the Gd(III) desorption contained much higher concentration of metals (components of sorbent) than the matrix solutions obtained after Gd(III) sorption. Besides, the spectrophotometric method based on the arsenazo III is much more selective than the technique with sulfarsazene. That is why we used this particular method to determine the content of the desorbed Gd(III) in the solution. The solutions absorbance was measured at λ=650 nm using a

spectrophotometer. In order to eliminate the interfering influence of Fe(III), Al(III), Mg(II) and Ca(II) ions, ascorbic and sulfosalicylic acids and Rochelle salt were additionally introduced into the system. The sorption and desorption were studied at the temperature of $20 \pm 1^\circ\text{C}$.

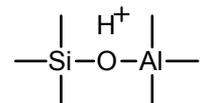
Results and discussion

The ion exchange occurs during the modification of clinoptilolite with an acid. Additionally, the dealumination of clinoptilolite is possible during this process. That is why the sorptive properties of acid-modified clinoptilolite depend on the concentration and origin of the acid used for modification. The features of this zeolite acid modification process were described elsewhere [10].

In order to study the influence of the concentration and origin of the acid on the zeolite modification, the sorption capacity of clinoptilolite samples modified with hydrochloric, nitric and sulfuric acid, solutions with different concentration was studied within 24 h. The result of this investigation demonstrated that the acid-modified sample obtained by the treatment of zeolite by 1 M H_2SO_4 solution ensured the most effective sorption of Gd(III) (Fig. 1).

The clinoptilolite samples treated with diluted solutions of hydrochloric (0.5 M) and nitric (1 M) acids proved to be efficient, similar to the case of sulfuric acid. The concentration of OH-groups, particularly silanol OH-groups, is increased during the acid modification of clinoptilolite. At the same time, the treatment of clinoptilolite with diluted (0.1–1.0 M) solutions of acids implies that the ionic exchange occurs with no significant dealumination

of the zeolite or any considerable change in its structure [10]. Moreover, along with this, the concentration of exchange protons increases and bridged hydroxyl groups of this type are formed as follows:



The surface OH-groups of zeolites are the most responsible for the heavy metals sorption. In this case, Al_2O_3 is located on the clinoptilolite grains surface and little parts of aluminooxygen tetrahedra are unstable in acid medium and can dissolve. During this acid modification of clinoptilolite, the part of Al(III) ions passes into the exchange complex of the sorbent. For example, the fraction of Al^{3+} ions in the exchange complex of the H-form of Transcarpathian clinoptilolite in the case of Cd(II) sorption is equal to $\sim 10\%$ [10]. In contrast to the doubly charged ions of d-elements, Gd(III) ions are more similar to Al(III) ions. Therefore, we think that the formation of the H-form of clinoptilolite with its structure preservation and Al^{3+} ions presence in the exchange complex results in an increase in the zeolite sorption efficiency towards Gd(III). Moreover, during this treatment, channels are also unlocked due to the dissolving of amorphous (i.e. non-carcess) Al_2O_3 . The acid-modified clinoptilolite samples obtained by their treatment by 1 M H_2SO_4 solution were used in our further investigations.

The influence of solution acidity on the sorption of Gd(III) ions on H-clinoptilolite was studied (Fig. 2). The appropriate pH values of gadolinium salt solutions were supplied by the addition of diluted

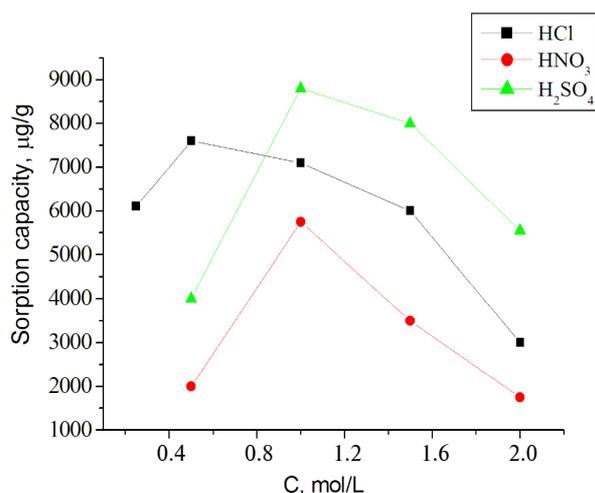


Fig. 1. Dependence of the sorption capacity of acid-modified clinoptilolite towards Gd(III) on the concentration of hydrochloric (1), nitric (2) and sulphuric (3) acids as modifiers. In all cases the Gd(III) concentration was $1.0 \mu\text{g/mL}$; pH 9.5

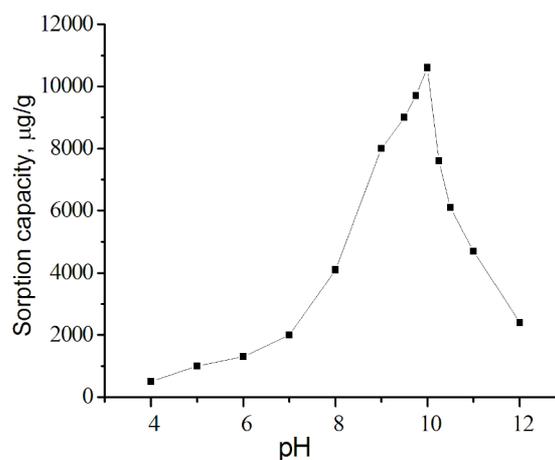


Fig. 2. Dependence of the sorption capacity of acid-modified clinoptilolite towards Gd(III) on the pH value of aqueous solution (the concentration of Gd(III) was $1.0 \mu\text{g/mL}$)

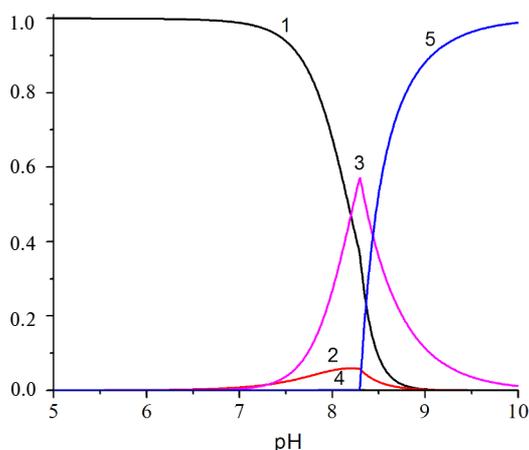


Fig. 3. Dependence of the Gd(III) species fraction on pH (the concentration of Gd(III) was 1.0 $\mu\text{g/mL}$): 1 – Gd^{3+} , 2 – GdOH^{2+} , 3 – Gd(OH)_2^+ , 4 – $\text{Gd}_2(\text{OH})_2^{4+}$, 5 – Gd(OH)_3

solutions of NaOH or HNO_3 . The most effective sorption was observed in the weak alkaline solutions (pH 10), where, according to our previous study [8], gadolinium(III) exists in Gd(OH)_3 form (Fig. 3). Therefore, the sorption of Gd(III) on H-clinoptilolite is achieved by the adsorption of soluble hydrolyzed forms of Gd(III) on the aluminosilicate surface.

The samples of Transcarpathian clinoptilolite in its natural form efficiently sorb the soluble Gd(OH)_3 hydrolyzed form from the weakly alkaline Gd(III) solutions [8]. In order to prove this fact, we investigated the influence of ethanol on the sorption capacity of clinoptilolite towards Gd(III). The Gd(III) ions is hydrolyzed in water-ethanol solutions much more than in water [13]. Considering this, the sorption efficiency of clinoptilolite towards Gd(III) trace amounts ($C_{\text{Gd(III)}}=1.0 \mu\text{g/mL}$) from aqueous and water-ethanol solutions was studied at pH 9.5 and pH 8.5.

Gd(III) is almost completely in Gd(OH)_3 form in aqueous solutions with pH 9.5. The maximum sorption capacity of clinoptilolite was observed in such solutions [8]. The sorption capacity of clinoptilolite at pH 9.5 is the same in aqueous and water-ethanol (25% $\text{C}_2\text{H}_5\text{OH}$) solutions (Table 1). At the same time, the sorption efficiency of clinoptilolite in water-ethanol solution with pH 8.5 increases more than by 30% than in Gd(III)-containing aqueous solution with pH 8.5. Only about 40% of Gd(III) trace amounts in aqueous solutions with pH 8.5 are in Gd(OH)_3 form (Fig. 3). The content of Gd(OH)_3 hydrolyzed form increases in Gd(III) water-ethanol solution with the same acidity, and therefore an increase in the sorption capacity of zeolite is observed. However, the Gd(III) trace

amounts are already almost completely in Gd(OH)_3 form in aqueous solution at pH 9.5 (Fig. 3). That is why the sorption capacity of clinoptilolite does not change with the additions of $\text{C}_2\text{H}_5\text{OH}$ to the Gd(III) solution at this acidity.

Table 1
Sorption capacity of clinoptilolite towards Gd(III) in water-ethanol solutions (the concentration of Gd(III) was 1.0 $\mu\text{g/mL}$)

pH	Sorption capacity, $\mu\text{g/g}$	
	without $\text{C}_2\text{H}_5\text{OH}$	25% (V/V) $\text{C}_2\text{H}_5\text{OH}$
9.5	6500	6500
8.5	4000	5300

The obtained results (Table 1) are also interesting in terms of the selective preconcentration of Gd(III) in the presence of $\text{C}_2\text{H}_5\text{OH}$. The presence of 25% (V/V) $\text{C}_2\text{H}_5\text{OH}$ does not affect the value of clinoptilolite sorption capacity under optimal conditions of Gd(III) sorption from solutions with pH 9.5. It is known that the authenticity of vintage wines is sometimes determined by the presence of Gd and other REEs [14]. That is why the Transcarpathian clinoptilolite can be promisingly used for the preparation of wine samples, in particular for the preconcentration of Gd(III) before analysis on the REEs content.

Earlier we have established [15] that the acid-modified clinoptilolite almost does not sorb another element of yttrium subgroup, such as Tb(III) at pH 11, whereas a rather high sorption capacity of clinoptilolite was observed with respect to Gd(III) at such values of pH (Fig. 2). These differences in sorption efficiency of acid-modified clinoptilolite towards Gd(III) and Tb(III) give the opportunity to pre-concentrate Gd(III) in the presence of Tb(III) and separate these lanthanides from the solutions at pH 11.0.

The buffer solutions were used to maintain the constant value of pH and ionic strength of the solutions and to improve the metrological characteristics of preconcentration method with respect to Gd. The Gd(III) trace amounts are most efficaciously sorbed in borate buffer solution. In $1.5 \cdot 10^{-4}$ M borate buffer solution (pH 10.0), the maximum value of sorption capacity of H-form of clinoptilolite towards Gd(III) is equal to 70% of the sorption capacity that is reached in the Gd(III)-containing solution at pH 10.0 supplied by NaOH solution.

The sorption capacity of acid-modified Transcarpathian clinoptilolite decreases with increasing the concentration of Gd(III) in the

solution (Table 2). Similar dependence were earlier found for clinoptilolite towards Tb and Pr [9,11]. These results can be associated with different abilities of Gd(III) ions to form hydroxo-complexes at low and high concentrations.

Table 2
Dependence of the sorption capacity of H-clinoptilolite on Gd(III) concentration (pH 10.0, $1.5 \cdot 10^{-4}$ M borate buffer solution)

Concentration of Gd(III), $\mu\text{g/mL}$	Sorption capacity, $\mu\text{g/g}$
0.5	8200
1.0	7500
5.0	5000
10.0	3600

Sorptive properties of natural form and H-form of Transcarpathian clinoptilolite depend significantly on their preliminary thermal treatment [8–11,15]. The corresponding data are shown in Fig. 4.

It can be seen that the sorption capacity of the uncalcined H-clinoptilolite is maximal (Fig. 4). The preliminary calcination of the acid-modified clinoptilolite at 150°C deteriorates its adsorption properties with respect to Gd(III) ions. A partial amorphization of the H-form of clinoptilolite is possible in this temperature range [10]. This may be the reason for a decrease in its sorption efficiency. The surface OH-groups are mainly the adsorption-active centers of various forms of Transcarpathian clinoptilolite towards metal ions [8–11]. A drastic increase in the sorption efficiency of H-clinoptilolite samples calcined at the temperature of 300°C is due

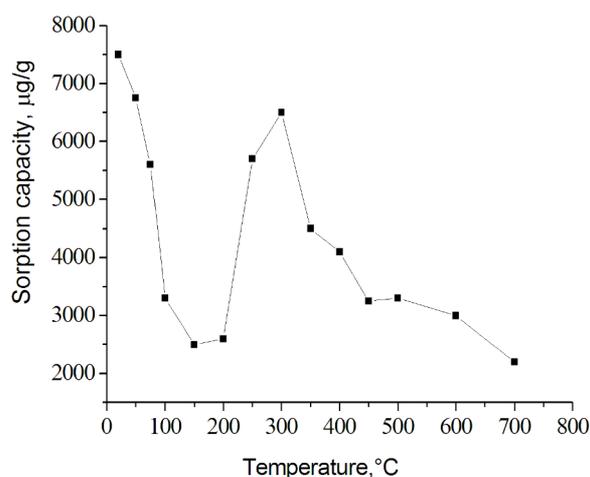


Fig. 4. Dependence of the sorption capacity of acid-modified clinoptilolite towards Gd(III) upon the temperature of thermal pretreatment (the concentration of Gd(III) was $1.0 \mu\text{g/mL}$; pH 10.0; $1.5 \cdot 10^{-4}$ M borate buffer solution)

to the growth of the surface OH-groups in the zeolite structure [10].

A further rapid decrease in the H-clinoptilolite sorption capacity in the temperature range of $350\text{--}450^\circ\text{C}$ can be explained by the processes of dehydroxylation of zeolites surface and its amorphization. The amorphization of H-clinoptilolite occurs most intensively exactly in this temperature range [10].

It was important to search for effective desorbents. The solutions of alkali metals (NaCl and KCl), acidified solutions of these salts and solutions of HCl were tested as desorbents. 1 M solution of HCl and 1 M solution of KCl acidified with HCl solution to pH 4.0 were preferred as desorbents of Gd(III) ions (Table 3), because they provided a full recovery of lanthanide.

Table 3
Desorption of gadolinium(III) from acid-modified clinoptilolite

Desorbent	Desorption, %
1 M KCl (acidified to pH 4.0 with HCl)	100
1 M NaCl (acidified to pH 4.0 with HCl)	90
1 M KCl	75
1 M NaCl	65
0.5 M KCl	70
1 M HCl	100
0.1 M HCl	75
10^{-4} M HCl	10

The influence of some «common» ions from natural and waste waters on the gadolinium(III) sorption by H-form of clinoptilolite was also investigated (Table 4). It can be seen that the sorption of Gd(III) trace amounts on this sorbent can be carried out against a background of main macrocomponents of waters.

Table 4
Permissible multiple contents of admixtures for gadolinium(III) sorption from aqueous solution of H-clinoptilolite (the concentration of Gd(III) was $1.0 \mu\text{g/mL}$; pH 10.0)

Admixture	Permissible multiple content
Na^+	1200
K^+	1000
Mg^{2+}	150
Ca^{2+}	30
NH_4^+	100
Cl^-	1000
NO_3^-	1500
SO_4^{2-}	1000

Taking into account a high sorption capacity of the acid-modified Transcarpathian clinoptilolite, its ability to sorb both low and high concentrations of Gd(III), the existence of efficient desorbents and the possibility to sorb Gd(III) in the presence of other ions, we can suggest this sorbent to recover Gd(III) from aqueous solutions and pre-concentrate Gd(III) ions at the stage of the preparation water samples for the analysis.

The proposed method of the preconcentration of Gd(III) trace amounts in the solid phase involves its further determination by means of spectrophotometric method with arsenazo III.

Technique of spectrophotometric determination of Gd(III):

0.5–2.0 L of the analyzed water was acidified by nitric acid to achieve pH~1, and then heated in the sand bath for 1 h. After filtration through the dense paper filter «blue ribbon», the pH of the water was adjusted to 7 with a solution of NaOH, and then a borate buffer solution with pH 10.0 was added. The concentration of the borate buffer in the final volume should be equal to $1.5 \cdot 10^{-4}$ M. Then, this solution was passed through the SPE cartridge filled with 0.6 g of the H-clinoptilolite using the peristaltic pump with the flow rate of 3 mL/min. After that, 50 mL of bidistilled water were passed through the cartridge with the same flow rate. Gadolinium(III) ions were desorbed by 15 mL of 1 M HCl at the flow rate of 0.5 mL/min. The eluate was collected in the 25 mL volumetric flask. 5 Milliliters of bidistilled water were added to the eluate, the solution was mixed and the pH value was adjusted to pH ~1 using 1 M solution of HCl. The solution volume in the volumetric flask was filled to the mark by bidistilled water and mixed.

The Gd(III) content in the solution was determined using the spectrophotometric method with arsenazo III. To this end, 2 mL of just-prepared 1% ascorbic acid solution were added to the solution of gadolinium (pH 1.0). In 2 min, 4 mL of the solution of 5% sodium potassium tartrate, 5 mL of the solution of 5% sulfosalicylic acid, 1 mL of the solution of formic buffer (pH 3.5) and 4 mL of the solution of 0.05% arsenazo III were added. The volume of the obtained solution was adjusted to 40 mL with distilled water and the pH was fixed at 2.6 ± 0.1 . The solution was transferred to a volumetric flask and its volume was adjusted to 50 mL. Then the solution absorbance was measured at 650 nm by using a DR/4000 V Spectrophotometer (HACH). The solution contained all above-mentioned components, except Gd(III), was used as a blank solution.

The proposed method of the Gd(III) preconcentration and determination was tested in the analysis of tap water with the additional input of Gd(III) ions. The results of the analysis are listed in Table 5.

Table 5
Determination of gadolinium(III) ions in the tap water with an additional introduction of Gd(III) ions after preconcentration with acid-modified clinoptilolite (n=3, P=0.95)

Volume of water sample (mL)	Enrichment factor ^a	Concentration of Gd(III), µg/mL		Recovery, %	RSD, %
		Added	Found		
600	40	1.00	0.98±0.04	98	1.63
1050	70	0.50	0.49±0.04	98	3.26
1500	100	0.10	0.101±0.010	101	3.96
1500	100	0.05	0.047±0.006	94	5.62
1950	130	0	N.D. ^b	–	–

Note: ^a – enrichment factor=volume of sample/volume of eluent; ^b – N.D. stands for «less than the detection limit».

Conclusions

The results obtained in this work confirmed that the acid-modified Transcarpathian clinoptilolite is an effective sorbent for the solid phase extraction of trace amount of Gd(III) from aqueous solutions. 1 M H₂SO₄ solution is the most effective acid-modifier. The H-form of clinoptilolite obtained without any significant dealumination is suitable for the preconcentration of Gd(III). The sorption capacity of H-clinoptilolite towards Gd(III) under the optimal conditions was 8.2 mg/g, which exceeded the sorption capacity of natural clinoptilolite towards this REE by ~30%. The conditions of desorption of gadolinium from the acid-modified clinoptilolite was investigated. The solutions of 1 M HCl and 1 M KCl acidified to pH 4.0 with HCl are the best desorbents of Gd(III), they allow adsorbing almost all Gd(III) preconcentrated on the zeolite. The proposed method for the determination of Gd(III) demonstrates a low detection limit and good RSD values. It can be successfully used for the determination of trace amounts of gadolinium ions in the presence of the majority of components of water.

Acknowledgments

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СОРБЦІЯ ГАДОЛІНІЮ НА КИСЛОТНО МОДИФІКОВАНОМУ КЛІНОПТИЛОЛІТІ

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Досліджено сорбційні властивості кислотно модифікованого закарпатського кліноптилоліту стосовно Gd(III) в динамічних умовах. Сорбційна ємність H-форми кліноптилоліту залежить від природи і концентрації кислоти-модифікатора. Найефективнішою кислотою-модифікатором є 1 М H₂SO₄. Сорбційна ємність H-форми закарпатського кліноптилоліту стосовно Gd(III) суттєво залежить від концентрації та рН розчину солі гадолінію, а також від температури попереднього прожарювання сорбенту. За оптимальних умов (діаметр зерен сорбенту 0,20–0,31 мм; швидкість пропускання розчину Gd(III) з концентрацією 0,5 мкг/мл через сорбент 5 мл/хв; рН 10,0) сорбційна ємність H-кліноптилоліту становить 8,2 мг Гадолінію на 1 г сорбенту. Сорбція слідових кількостей Gd(III) H-кліноптилолітом відбувається на фоні поширених у воді іонів. Найефективнішими десорбентами Gd(III), що сконцентровані на H-формі кліноптилоліту, є розчини 1 М HCl та 1 М KCl, підкислені HCl до рН 4,0. Розроблений метод концентрування слідових кількостей гадолінію з водних розчинів у режимі твердофазової екстракції з подальшим визначенням цього рідкісноземельного елемента спектрофотометричним методом. Межа виявлення цього методу становить 0,3 нг/мл, а лінійність оцінювали в діапазоні 1–200 нг/мл.

Ключові слова: гадоліній, сорбція, концентрування, H-кліноптилоліт, твердофазова екстракція.

SORPTION OF GADOLINIUM ON ACID-MODIFIED CLINOPTILOLITE

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The sorptive properties of the acid-modified Transcarpathian clinoptilolite towards Gd(III) under dynamic conditions were investigated. The sorption capacity of the clinoptilolite in H-form depends on the nature and concentration of acid-modifier. The most effective sorption of Gd(III) was observed when clinoptilolite was pretreated with 1 M H₂SO₄ solution. The sorption capacity of the H-form of Transcarpathian clinoptilolite towards Gd(III) significantly depends on the concentration of gadolinium salt, the pH of solution and the temperature of the preliminary calcination of the sorbent.

The sorption capacity of H-clinoptilolite under optimal conditions (diameter of zeolite grains was 0.20–0.31 mm; flow rate of gadolinium(III) solution with concentration 0.5 µg/mL through sorbent was 5 mL/min; and pH 10.0) was 8.2 mg gadolinium per 1 g of acid-modified clinoptilolite. The H-clinoptilolite sorbs the Gd(III) trace amounts even in the presence of other common ions. The solutions of 1 M HCl and 1 M KCl acidified by a hydrochloric acid to pH 4.0 are the most effective desorbents of gadolinium(III) ions from H-clinoptilolite. The method for gadolinium trace amounts preconcentration from aqueous solutions in a solid phase extraction mode with a further determination of this rare earth element by a spectrophotometric method was developed. The detection limit of this method is 0.3 ng/mL, and the linearity was evaluated in the range of 1–200 ng/mL.

Keywords: gadolinium; sorption; preconcentration; H-clinoptilolite; solid phase extraction.

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