

Article

# Solid Phase Extraction of Trace Amounts of Praseodymium Using Transcarpathian Clinoptilolite

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**Abstract:** Sorptive properties of the Transcarpathian clinoptilolite towards Pr(III) were studied under dynamic conditions. The sorption capacity of clinoptilolite under optimal conditions (sorbent grain diameter of 0.20–0.31 mm; pH 9.0, temperature of preliminary precalcination of 350 °C, and flow rate of the Pr(III) salt solution with the concentration of 1.0 µg·mL<sup>-1</sup> through the sorbent of 5 mL·min<sup>-1</sup>) was equal to 47.5 mg·g<sup>-1</sup>. The best desorbent of Pr from the clinoptilolite was the 1 M solution of KCl acidified with HCl to a pH value of 3.0. The method of Pr(III) trace amounts preconcentration in a solid phase extraction mode with further determination of this REE via spectrophotometric technique was developed. The linearity of the proposed method was evaluated in the range of 2–100 ng·mL<sup>-1</sup> with detection limit of 0.7 ng·mL<sup>-1</sup>.

**Keywords:** preconcentration; sorption; lanthanide; natural zeolite

## 1. Introduction

Lanthanides (Ln) possess unique chemical and physical properties, which lead to their wide applications in different branches of industry. As for praseodymium, its overall quantity in the Earth's crust is low. This rare Earth element (REE) is applied in electronics, laser systems, nuclear power engineering, etc. Praseodymium is a component of alloys for the preparation of magnets, aviation engines, and electrodes. It is also a constituent of the optical glasses. The estimation of praseodymium and other REE content has been used for the authentication of trademark wines [1]. The analysis of different objects in terms of this lanthanide content is often problematic. Determination of trace amounts of REEs in geological, biological and environmental samples is one of the most difficult tasks, because of the similarity of their chemical behaviors. Methods of Pr determination mostly require a thorough sample pretreatment, which includes preconcentration, separation and withdrawal of this Ln. In recent years, the method of solid phase extraction is used in sample preparation for analysis because of its high recovery, high enrichment factor, rapid phase separation, application of small volumes of organic solvents and low cost [2]. This method of samples pre-treatment is demanded even during the analysis of samples with such selective and highly sensitive methods as energy dispersive X-ray fluorescence and inductively coupled plasma [3–8]. The exclusion and regeneration of praseodymium from technological solution is also significant. The solution to these problems is to a large extent connected with the application of efficient selective sorbents of this lanthanide.

Various sorbents are used for praseodymium preconcentration via solid phase extraction technique, such as modified silica gel [3,4], carbon-ferrite magnetic nanocomposite [5], Muromac A-1 resin [6], Chromosorb 106-TAR resin [7], and Fe<sub>3</sub>O<sub>4</sub>@TiO<sub>2</sub>@P<sub>2</sub>O<sub>4</sub> nanoparticles [8]. Xiong et al. [9] studied the adsorption of Pr(III) from aqueous solutions using strongly acidic cation exchange resin

D72. Methods for praseodymium(III) preconcentration from the nitrate medium using TVEX-PHOR resin [10] and synthetic zeolite [11] are proposed. Natural zeolites are also efficient sorbents of REEs. They have many advantages in comparison to other ones. Unlike many other natural aluminosilicates, zeolites exhibit high sorption ability at a low concentration of a substance being sorbed, have good stability in aggressive medium and under thermal treatment, selectivity, possibility of easy modification of the sorbent, and low cost. To the best of our knowledge, investigations of natural zeolite sorption properties towards Pr(III) practically have not been carried out yet. It is only known that clinoptilolite has been applied for the decontamination of waste waters that contained the  $^{144}\text{Pr}$  isotope [12]. This adsorbent is the most common among all natural zeolites. It is often used as a sorbent in the solid phase extraction method [13–17].

The aim of this work was to study the sorption properties of Transcarpathian clinoptilolite towards trace amounts of Pr(III) in aqueous solutions and to investigate the possibility of this natural sorbent application in the solid phase extraction method.

## 2. Materials and Methods

### 2.1. Reagents and Apparatus

All reagents were of analytical grade. Standard aqueous solutions of praseodymium nitrate (concentration:  $1.0 \text{ mg mL}^{-1}$ ) were prepared by dissolving the metallic praseodymium (99.9% purity) in the nitric acid solution (1:1). The working solutions of Pr(III) were prepared by the appropriate dilution of the standard solution. The 0.05% solution of sulfarsazene was prepared using 0.05 M aqueous solution of  $\text{Na}_2\text{B}_4\text{O}_7$ ; all other reagent solutions used bidistillate. Borate buffer solution with pH 9.0 was prepared by mixing together 85 mL of 0.05 M  $\text{Na}_2\text{B}_4\text{O}_7$  solution with 15 mL of 0.1 M HCl. Tris-buffer solution with pH 9.0 was prepared by mixing 25 mL of 0.2 M Tris solution with 0.1 M solution of HCl and filling the mixture volume to 1.0 L with bidistilled water.

The clinoptilolite from the deposit in the village of Sokyrnytsia, situated in the Zakarpattia region of Ukraine contained 85–90% (mass fraction) of the main component. Its specific surface area, determined by water sorption, was equal to  $59 \text{ m}^2 \cdot \text{g}^{-1}$  [18]. The clinoptilolite formula in the oxide form (mass fraction) is as follows:  $\text{SiO}_2$ , 67.29;  $\text{Al}_2\text{O}_3$ , 12.32;  $\text{TiO}_2$ , 0.26;  $\text{Fe}_2\text{O}_3$ , 1.26; FeO, 0.25; MgO, 0.99; CaO, 3.01;  $\text{Na}_2\text{O}$ , 0.66;  $\text{K}_2\text{O}$ , 2.76;  $\text{H}_2\text{O}$ , 10.90 [19].

The thermal heating of Transcarpathian clinoptilolite was carried out for 2.5 h in the oven. Spectrophotometric determination was carried out on a HACH DR/400 V spectrophotometer. A 150-MI pH meter was used for pH measurements.

### 2.2. Sorption Studies

The sorption properties of clinoptilolite were studied under dynamic condition using a peristaltic pump. The solution of Pr(III) salt was passed through a cartridge for preconcentration filled with 0.6 g of the sorbent at a flow rate of  $5 \text{ mL min}^{-1}$ . The clinoptilolite with a grain size of 0.20–0.31 mm was used. The investigation techniques under dynamic conditions are described in detail in [20]. The passage point of praseodymium(III) was registered spectrophotometrically using the reaction that leads to a formation of orange complex of praseodymium(III) with sulfarsazene. Sulfarsazene changes its color from yellow to orange starting from the praseodymium(III) concentration of  $100 \text{ ng} \cdot \text{mL}^{-1}$ . This gave the opportunity to determine the passage moment of Pr(III) using a spectrophotometer at 540 nm.

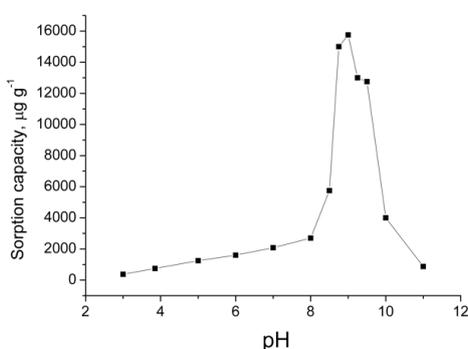
The desorption of Pr(III) pre-concentrated on clinoptilolite was carried out by passing 15 mL of a desorbent solution through the preconcentration cartridge with a flow rate of  $0.5 \text{ mL} \cdot \text{min}^{-1}$ . The eluate was collected in a 25 mL volumetric flask and filled up to the mark with bidistilled water. As pre-acidified solutions of alkali metals are efficient desorbents of Pr(III) from clinoptilolite, the solutions obtained after the desorption of Pr(III) contained much higher concentration of metals that are constituents of the sorbent than the matrix solutions obtained after Pr(III) sorption on clinoptilolite.

That is why the selectivity of Pr(III) spectrophotometric determination with sulfarsazene proved to be not enough during the analysis of eluates obtained after the desorption of Pr(III). Thus, to determine the content of desorbed Pr(III) in a solution, the spectrophotometric technique based on arsenazo III [21] was applied, which, despite being less sensitive, is much more selective than the technique with the application of sulfarsazene. The solutions absorbance was measured at  $\lambda = 650$  nm on a spectrophotometer. The adsorption and desorption studies were carried out at  $20 \pm 1$  °C.

### 3. Results and Discussion

#### 3.1. Effect of pH on Sorption

The sorption of praseodymium(III) on clinoptilolite depending on the medium acidity was studied (Figure 1). The necessary pH values of praseodymium salt solutions were supplied by adding diluted solutions of NaOH or HNO<sub>3</sub>. Pr(III) was sorbed most efficiently from the weakly alkaline solutions. On the curve showing this dependence, a clear maximum at pH 9.0 was observed.



**Figure 1.** Dependence of the sorption capacity of clinoptilolite towards praseodymium(III) on the pH value of the aqueous solution (concentration of Pr(III):  $1.0 \mu\text{g}\cdot\text{mL}^{-1}$ ).

To supply the constant pH and the ionic strength of solutions, the application of Tris-buffer solution with pH 9.0 was proposed. The sorption capacity of clinoptilolite towards Pr(III) does not change in the medium of this buffer solution. The application of borate buffer solution decreases the sorption capacity of zeolite by 30%.

Such Pr(III) sorption process is caused by the chemical peculiarities of clinoptilolite surface and by existing forms of Pr(III) in solutions. It is known [15–18] that mainly the surface OH-groups of Transcarpathian clinoptilolite are the sorption-active centers towards heavy metal ions. Usually, heavy metals are more efficiently sorbed by a zeolite from weakly alkaline solutions when the dissociation of hydroxyl groups on the grains surface of a mineral takes place. At the same time, the Pr(III) existing form in a solution changes while varying the pH. The distribution of different forms of Pr(III) in aqueous solutions in the pH range from 2 to 12 at different total concentration of the metal ( $1.77 \times 10^{-6}$  and  $7.09 \times 10^{-6}$  M) was calculated.

The system of equations that describes equilibria of Pr(III) hydrolysis is the following:

$$K_{11} = \frac{[\text{PrOH}^{2+}][\text{H}^+]}{[\text{Pr}^{3+}]} \quad (1)$$

$$K_{12} = \frac{[\text{Pr}(\text{OH})_2^+][\text{H}^+]^2}{[\text{Pr}^{3+}]} \quad (2)$$

$$K_{22} = \frac{[\text{Pr}_2(\text{OH})_2^{4+}][\text{H}^+]^2}{[\text{Pr}^{3+}]^2} \quad (3)$$

$$C_{\text{Pr}} = [\text{Pr}^{3+}] + [\text{PrOH}^{2+}] + [\text{Pr}(\text{OH})_2^+] + 2[\text{Pr}_2(\text{OH})_2^{4+}] + [\text{Pr}(\text{OH})_3] \quad (4)$$

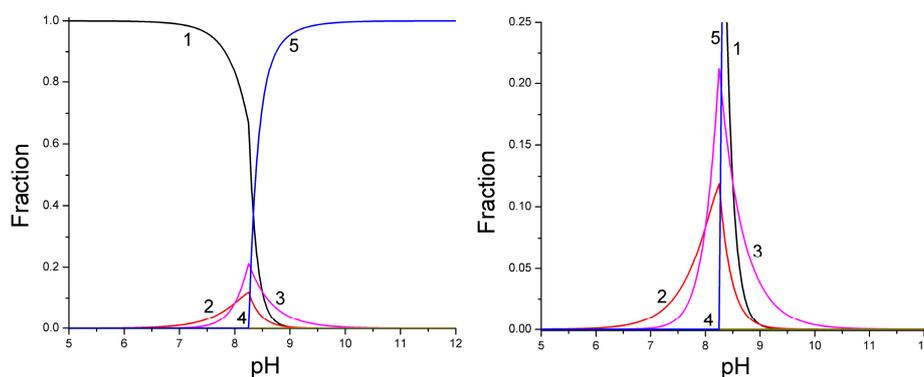
$$K_s \geq [\text{Pr}^{3+}][\text{OH}^-]^3 \quad (5)$$

During the calculations, it was assumed that total praseodymium hydroxide  $\text{Pr}(\text{OH})_3$  (if it actually formed) exists in a solution and the formation of a solid phase is not observed.

As it was not clear whether the formation of  $\text{Pr}(\text{OH})_3$  took place (i.e., whether the  $K_s$  condition was fulfilled), the solution of equations system was carried out in two stages. First, it was assumed that the condition of  $\text{Pr}(\text{OH})_3$  formation was not fulfilled, thus the equilibrium state was calculated assuming that  $[\text{Pr}(\text{OH})_3] = 0$ . At this stage, the equilibrium concentrations of  $\text{Pr}^{3+}$  and  $\text{PrOH}^{2+}$  forms were found for each pH value. Then, the condition of the neutral hydroxide formation ( $[\text{Pr}^{3+}] \cdot [\text{OH}^-]^3 \geq K_s$ ) was checked for each pH value. If the condition was fulfilled, the solution of equations system was carried out considering the expression for  $K_s$  and the equilibrium concentration of  $\text{Pr}(\text{OH})_3$  was also determined. In the conditions of our investigations, the concentration of foreign electrolytes did not exceed  $0.01 \text{ mol} \cdot \text{L}^{-1}$ , thus the averaged constants values found at low ionic strength of a solution ( $\mu < 0.01$ ) were used for calculations [22–24]. The graphs of Pr(III) different species distribution at various concentrations of this lanthanide are presented on Figures 2 and 3.

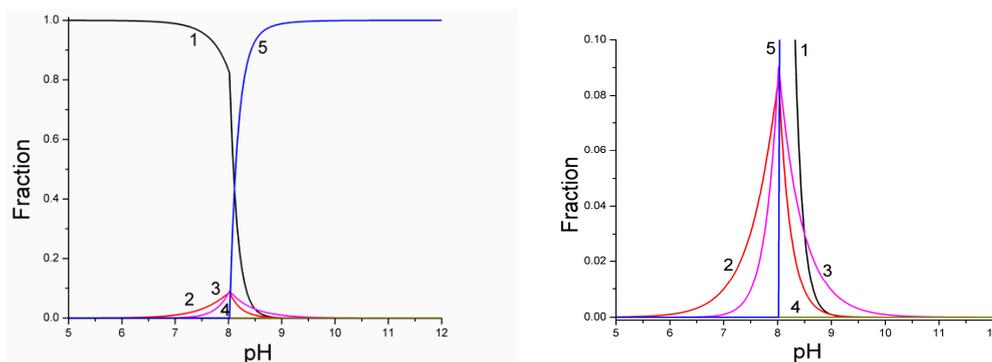
According to the calculations, it was established that at Pr(III) concentration of  $1.77 \times 10^{-6} \text{ M}$  at  $\text{pH} < 6.5$  almost all metal content remained in  $\text{Pr}^{3+}$  form, and at  $\text{pH} > 10$  it was completely in  $\text{Pr}(\text{OH})_3$  form (Figure 2). The formation of  $\text{Pr}(\text{OH})_3$  occurred at  $\text{pH} > 8.25$  and starting from  $\text{pH} 9.6$  its fraction reached 99%.

At higher total concentration of Pr(III) ( $7.09 \times 10^{-6} \text{ M}$ ) at  $\text{pH} < 6$ , the metal almost completely existed in  $\text{Pr}^{3+}$  form, and at  $\text{pH} > 9.5$  it was completely in  $\text{Pr}(\text{OH})_3$  form (Figure 3). The formation of  $\text{Pr}(\text{OH})_3$  took place at lower pH values ( $> 8.02$ ) and starting from  $\text{pH} 9.05$  its molar fraction reached 99%.



**Figure 2.** Dependence of the Pr(III) species fraction on pH (concentration of Pr(III):  $1.77 \times 10^{-6} \text{ M}$ ) (1,  $\text{Pr}^{3+}$ ; 2,  $\text{PrOH}^{2+}$ ; 3,  $\text{Pr}(\text{OH})_2^+$ ; 4,  $\text{Pr}_2(\text{OH})_2^{4+}$ ; 5,  $\text{Pr}(\text{OH})_3$ ).

At such low total concentrations of the metal (Figures 2 and 3), the formation of the  $\text{Pr}_2(\text{OH})_2^{4+}$  specimen was not detected (at the total concentration of Pr(III)  $1.77 \times 10^{-6} \text{ M}$ , the maximal fraction appeared at  $\text{pH} 8.25$  and did not exceed  $2.45 \times 10^{-4}\%$ ; and at the total concentration of Pr(III)  $7.09 \times 10^{-6} \text{ M}$ , the maximal fraction appeared at  $\text{pH} 8.02$  and did not exceed  $5.2 \times 10^{-4}\%$ ), thus its formation could be neglected. At the same pH value, the maximal quantities of  $\text{PrOH}^{2+}$  and  $\text{Pr}(\text{OH})_2^+$  forms were observed. In particular, at the total concentration of Pr(III)  $1.77 \times 10^{-6} \text{ M}$ , the fraction of  $\text{PrOH}^{2+}$  was equal to 11.9%, and  $\text{Pr}(\text{OH})_2^+$  21.2%. While increasing the total concentration of Pr(III) to  $7.09 \times 10^{-6} \text{ M}$ , the fractions of these forms decreased ( $\text{PrOH}^{2+}$  to 8.6% and  $\text{Pr}(\text{OH})_2^+$  to 9.0%). As soon as pH reached the value that corresponded to the formation of a neutral  $\text{Pr}(\text{OH})_3$ , molar fractions of these species decreased drastically.



**Figure 3.** Dependence of the Pr(III) species fraction on pH (concentration of Pr(III),  $7.09 \times 10^{-6}$  M) (1,  $\text{Pr}^{3+}$ ; 2,  $\text{PrOH}^{2+}$ ; 3,  $\text{Pr}(\text{OH})_2^+$ ; 4,  $\text{Pr}_2(\text{OH})_2^{4+}$ ; 5,  $\text{Pr}(\text{OH})_3$ ).

The highest sorption capacity value of clinoptilolite towards Pr(III) was reached in weakly alkaline solutions with pH 9.0 (Figure 1). At the total concentration of Pr(III) comparable to its concentration in solutions that were used to study the sorptive properties of clinoptilolite, Pr(III) in the solution with pH 9.0 usually existed in the  $\text{Pr}(\text{OH})_3$  form (~99%) and partially in the  $\text{Pr}(\text{OH})_2^+$  form (~1%) (Figure 3). Thus, the sorption of Pr(III) on Transcarpathian clinoptilolite took place mainly through the adsorption of the soluble neutral Pr(III) hydroxide on the aluminosilicate surface. Such assumption was confirmed by the fact that the sorption capacity of clinoptilolite increased drastically starting from pH ~ 8.0, i.e. from the moment when the formation of  $\text{Pr}(\text{OH})_3$  began.

### 3.2. Effect of Concentration

It was determined that the sorption capacity of Transcarpathian clinoptilolite decreased while increasing the concentration of Pr(III) in the solution (Table 1). We assumed that different sorptive capability of the zeolite towards low and high concentrations of Pr(III) is due to the different ability to form hydroxo-complexes at low and high concentrations.

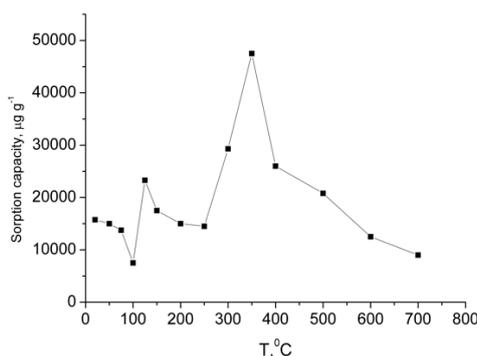
**Table 1.** Dependence of the sorption capacity of clinoptilolite on concentration of Pr(III), pH 9.0.

Concentration of Pr(III), $\mu\text{g}\cdot\text{mL}^{-1}$	Sorption Capacity, $\text{mg}\cdot\text{g}^{-1}$
0.25	21.5
0.5	20.5
1.0	15.8
5.0	12.0
10.0	4.0

The data obtained show that, at sorption optimal conditions (pH 9.0), Pr(III) mainly existed in a form of neutral hydrolyzed  $\text{Pr}(\text{OH})_3$  and partly as  $\text{Pr}(\text{OH})_2^+$ . This evidences that clinoptilolite sorbs most efficiently the hydrolyzed neutral form  $\text{Pr}(\text{OH})_3$  and partly the cationic hydrolyzed form  $\text{Pr}(\text{OH})_2^+$ . Data in Table 1 evidence that, during the increase of Pr(III) concentration, the sorption capacity decreased. In our opinion, this was caused by the decrease of the hydrolyzed cationic form  $\text{Pr}(\text{OH})_2^+$  fraction with the increase of Pr(III) concentration. In particular, at the total Pr(III) concentration of  $1.77 \times 10^{-6}$  M ( $0.25 \mu\text{g}\cdot\text{mL}^{-1}$ ), the fraction of  $\text{Pr}(\text{OH})_2^+$  in the solution was equal to ~ 5% (Figure 2). At the total concentration of Pr(III) of  $7.09 \times 10^{-6}$  M ( $1 \mu\text{g}\cdot\text{mL}^{-1}$ ), the fraction of  $\text{Pr}(\text{OH})_2^+$  in the solution was equal to ~1% (Figure 3).

### 3.3. Effect of Thermal Treatment of Sorbent

Sorptive properties of Transcarpathian clinoptilolite depend significantly on its preliminary thermal treatment [15–18,25–29]. The results obtained are shown on Figure 4.



**Figure 4.** Dependence of the sorption capacity of clinoptilolite towards praseodymium(III) on thermal treatment.

The preliminary calcination of clinoptilolite at 100 °C led to a significant decrease of its sorption capacity towards Pr(III). It is known [26] that at such temperature the evaporation of the liquid water surface layer takes place. This process probably caused the decrease of sorption capacity of clinoptilolite samples pre-calcined at 100 °C in comparison with the uncalcined samples. The main maximum at the temperature of 350 °C was clearly visible on the curve showing the dependence of clinoptilolite sorption capacity towards Pr(III) on the temperature of the sorbent thermal pretreatment (Figure 4). The clinoptilolite samples pre-calcined at such temperature had the highest value of specific surface area ( $86 \text{ m}^2 \cdot \text{g}^{-1}$ ) [17], which, probably caused the increase of sorption capacity. The sorption capacity of clinoptilolite calcined at 350 °C towards Pr(III) was equal to  $47.5 \text{ mg} \cdot \text{g}^{-1}$ , which significantly exceeded the sorption capacity of this zeolite towards most REEs [15,17,25,27–29].

We explain the decrease of clinoptilolite sorption capacity at temperatures  $>350$  °C as the processes of partial amorphization of the zeolite [18,30]. During the partial amorphization of clinoptilolite, partial changes in its structure take place [30], which lead to the decrease of the clinoptilolite fraction and consequently the sorbent of Pr(III) in zeolite samples calcined at temperatures  $>350$  °C.

### 3.4. Desorption

An important stage of the work was the search for effective desorbents. For this purpose, solutions of alkali metal salts (NaCl and KCl), acidified solutions of these salts and HCl solutions were tested. The desorption results (Table 2) testify that the best desorbent of praseodymium was the 1 M solution of KCl, acidified with HCl solution to pH 3.0.

**Table 2.** Desorption efficiency of Pr(III) from clinoptilolite.

Desorbent	Desorption, %
1 M KCl (acidified to pH 3.0 with HCl)	100
1 M KCl (acidified to pH 3.2 with HCl)	90
1 M KCl (acidified to pH 3.8 with HCl)	85
1 M NaCl (acidified to pH 3.8 with HCl)	75
1M KCl	55
1 M NaCl	45
HCl (pH 3.0)	10

### 3.5. Effect of Coexisting Ions

The influence of common ions from natural and waste waters on the preconcentration of praseodymium(III) with clinoptilolite was investigated. Permissible multiple contents ( $C_{\text{ion}}/C_{\text{Pr(III)}}$ ) of these ions did not change the maximum sorption capacity of clinoptilolite towards Pr(III) (Table 3). The sorption of Pr(III) trace amounts on this natural sorbent took place on the background of main macrocomponents of waters.

**Table 3.** Tolerance limits of some ions for praseodymium(III) sorption from aqueous solution of Transcarpathian clinoptilolite (concentration of Pr(III) = 1  $\mu\text{g}\cdot\text{mL}^{-1}$ ).

Ions	Tolerance Limit ( $C_{\text{ion}}/C_{\text{Pr(III)}}$ )
K <sup>+</sup>	600
Na <sup>+</sup>	600
NH <sub>4</sub> <sup>+</sup>	500
Mg <sup>2+</sup>	100
Ca <sup>2+</sup>	30
Cl <sup>-</sup>	1500
NO <sub>3</sub> <sup>-</sup>	1500
SO <sub>4</sub> <sup>2-</sup>	1000

### 3.6. Sample Preconcentration Procedure

The sorbent was prepared as follows: A sample of natural Transcarpathian clinoptilolite was grained in a ball-mill; a zeolite fraction with a grain size of 0.20–0.30 mm was taken and washed with distilled water. The dried at room temperature clinoptilolite was calcined in a muffle oven at 350 °C for 2.5 h. The sorbent was cooled in a desiccator. Then, 0.5–2.0 L of the investigated water was acidified with nitric acid to pH ~1, heated on the sand bath for 1 h, and then filtered through the dense paper filter “blue ribbon”. The solution of NaOH was added to the filtrate to pH ~7, and then the Tris-buffer solution with pH 9.0 was added. The concentration of the Tris-buffer in the final volume should be equal to  $3.5 \times 10^{-4}$  M. Then, this solution was passed through the preconcentration cartridge filled with 0.6 g of the sorbent using the peristaltic pump with the flow rate of 3 mL min<sup>-1</sup>. After that, 50 mL of bidistilled water were passed through the cartridge with the same flow rate. The desorption of Pr(III) was carried as follows: 15 mL of 1 M KCl solution, acidified with HCl to pH 3.0, were passed through the cartridge with a flow rate of 0.5 mL min<sup>-1</sup>. The eluate was collected in the 25.0 mL volumetric flask. Five milliliters of bidistilled water were added to the eluate, the solution was mixed and the pH value was adjusted to pH ~1 using the 1 M solution of HCl. The solution volume in the volumetric flask was filled to the mark by bidistilled water and mixed. The Pr(III) content in the solution was determined using the spectrophotometric method with arsenazo III.

### 3.7. Method of Spectrophotometric Determination with Arsenazo III

Two milliliters of just-prepared 1% solution of ascorbic acid were added to the investigated solution (pH~1); after 2 min, 4 mL of 5% sulfosalicylic acid solution, 5 mL of 5% potassium-sodium tartrate solution, 1 mL of the formic buffer solution with pH 3.5, and 4 mL of 0.05% arsenazo III solution, diluted with bidistilled water to ~ 40 mL, were mixed and the pH value was adjusted to  $2.6 \pm 0.1$ . The solution was transferred to a 50.0 mL volumetric flask, filled with bidistilled water to the mark, mixed and the absorbance of the colored solution was measured at 650 nm. As a blank, a solution that contained all components except Pr(III) was used (the solution of “idle” experiment). In general, the proposed method for determination of Pr(III) ions had a linearity range from 2 to 100 ng·mL<sup>-1</sup>. The detection limit was found to be 0.7 ng·mL<sup>-1</sup>.

The proposed method of Pr(III) preconcentration and determination was tested during the analysis of tap water with the additional input of Pr(III) ions. The results of the analysis are given in Table 4.

**Table 4.** Determination of praseodymium(III) ions in the tap water with an additional introduction of Pr(III) ions after preconcentration with clinoptilolite ( $n = 3$ ,  $P = 0.95$ ).

Volume of Water Sample (mL)	Enrichment Factor <sup>a</sup>	Concentration of Pr(III) ( $\mu\text{g}\cdot\text{mL}^{-1}$ )		Recovery (%)	RSD (%)
		Added	Found		
600	40	1.00	0.99 $\pm$ 0.05	99	2.02
600	40	0.50	0.50 $\pm$ 0.05	100	4.01
1500	100	0.10	0.098 $\pm$ 0.012	98	5.11
1500	100	0.05	0.051 $\pm$ 0.010	102	7.84
1950	130	0.02	0.019 $\pm$ 0.005	95	9.12
1500	100	0	N.D. <sup>b</sup>		

<sup>a</sup> Enrichment factor = volume of sample/volume of eluent; <sup>b</sup> N.D. < detection limit.

#### 4. Conclusions

The results of this investigation confirm that Transcarpathian clinoptilolite is an effective sorbent for the preconcentrate of trace amount of Pr(III) from aqueous solutions. Under the optimal conditions, the sorption capacity of clinoptilolite towards Pr(III) was equal to  $47.5 \text{ mg}\cdot\text{g}^{-1}$ , which significantly exceeded the sorption capacity of this zeolite towards most REEs. The ability of Transcarpathian clinoptilolite to sorb either low or high concentrations, its high sorption capacity, and the presence of the efficient desorbent give a reason to propose this common natural sorbent for the exclusion of Pr(III) ions during the stage of water preparation for analysis. The developed method of Pr(III) trace amounts preconcentration in a solid phase extraction mode with further determination of this REE by the spectrophotometric method using arsenazo III presented low detection limit, wide linear range, high enrichment factor and good RSD values. It can be successfully applied for determination of trace amounts of praseodymium ions in water.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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