

On-line Green Solid Phase Extraction of Trace Rare Earth Elements and Uranium in Environmental Samples and ICP OES Detection

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An on-line solid phase extraction (SPE) method using mini column packed with natural sorbent based on cotton roll dyed by quinalizarin was developed for simultaneously pre-concentration of rare earth elements and uranium at trace levels in environmental samples followed by inductively coupled plasma optical emission spectrometry (ICP OES) determination. Various parameters such as sample and eluent flow rate, sample volume and matrix ions on the method efficiency have been investigated. Under the optimized conditions, the limits of detection (LODs, 3σ) for rare earth elements were in the range of 0.002-0.300 $\mu\text{g L}^{-1}$ and 0.420 $\mu\text{g L}^{-1}$ for uranium. The relative standard deviation ($n = 5$) were lower than 6% except for samarium and uranium. The method was successfully applied for determination of trace rare earth elements and uranium in lake, well, tap water and carbonate mineral samples. The accuracy of the proposed method was validated by add-found method and direct analysis by ICP OES. This method has some advantages such as simplicity, rapidity, green chemistry and high sensitivity.

Keywords: on-line solid phase extraction, ICP OES, rare earth elements, uranium, quinalizarin

Introduction

Nowadays ground water globally has gained more paramount attention. For the protection and safe use of ground water, it is important to know the origin of water and how it is influenced by the environment. The chemical formulation of waters in the continental crust is determined by water-rock interaction. For inspection of this process fact, the rare earth elements (REEs) can be used as tracers. REEs are also of interest in a wide range of fields in geochemistry including magmatic, hydrothermal and low temperature environments.¹⁻³ These elements are also being widely used in high technology industries due to their metallurgical, optical and electronic properties.⁴⁻⁷ Rare earth elements enhance chlorophyll content and improve photosynthetic rate, so they have been applied as plant regulator for crops.⁸⁻¹⁰ The rising consumption of REEs in different industries have lead to the great amount discharge of them into the environment. The importance of rare earth elements at mentioned field demands their determination accurately and precisely. Recently, studies for determination of REEs

in natural water samples have increased greatly. Due to low content of REEs in water samples and complexity of matrix (e.g., marine samples) the most common sensitive analytical techniques used, are inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP OES).¹¹⁻¹⁷ Although ICP-MS has the detection power to determine traces elements at sub $\mu\text{g L}^{-1}$, it suffers from the problem of isobaric polyatomic interferences and its low tolerance to total dissolved solids (TDS). This technique is very expensive; its maintenance is very difficult and inaccessible for much laboratories.¹⁸ Low level of rare earth elements in natural water samples is not compatible with limits of detection (LOD) exhibited by ICP OES technique. Also, ICP OES sometimes encounters problems such as signal suppression and clogging of the introduction system as for dissolved solids in natural samples. For these reasons, there is a demand for pre-concentration and separation of REEs as a group from different matrices before determination. For matrix separation and pre-concentration of REEs, solid phase extraction (SPE) in off-line/on-line mode¹⁹⁻²⁵ has been usually used more than other separation techniques such as dispersive liquid-liquid microextraction (DLLME),²⁶

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co-precipitation²⁷ and cloud point extraction.²⁸ On-line SPE mode in comparison with off-line mode has greater efficiency, lower consumption of sample and reagent, improved precision and capability of on field sampling.^{29,30} On-line column pre-concentration systems coupled with ICP OES are based on retention of analytes in mini/micro column packed with adsorbent that determines the sensitivity and selectivity of the analytical method. The choice of an adsorbent material for SPE can provide simple operation and more flexible working conditions. Many kinds of solid materials for REEs have been reported in the literature.³¹⁻³⁴

Quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) is an organic compound which is one of many tetrahydroxyanthraquinone isomers that has been frequently utilized as an analytical reagent in metal ions and pharmaceutical analysis.^{35,36}

Our research group has previously reported an off-line methodology with octadecyl silica gel modified with quinalizarin prior to ICP OES determination of REEs.³⁷ In the present work, a simple on-line procedure for pre-concentration and determination of trace levels REEs and uranium (U) in natural water samples and carbonate mineral by ICP OES is proposed. The mini column is packed with cotton roll dyed by quinalizarin as sorbent material. The operation condition of ICP OES was optimized using experimental design (Box-Behnken)^{38,39} to get better signal to noise ratio.

Experimental

Instrumentation

Simultaneous ICP OES (Varian 735-ES, Palo Alto, CA, USA) in radial torch configuration equipped with V-groove nebulizer and charge coupled device (CCD) detector was used for elemental analysis. Control of the spectrometer was provided by PC-based ICP Expert II software (Agilent Technologies, Santa Clara, CA, USA). For pH adjustment a Jenway 3510 pH meter (Staffordshire, UK) was used. A four channel peristaltic pump (accompanying ICP OES instrument) and a six-port rotary valve were used for coupling SPE extraction system to ICP OES instrument.

Standard solution and reagents

Working standard solutions by further dilution of stock REEs and U solution ($100 \mu\text{g mL}^{-1}$; SM 80B-500 VHG Labs, Manchester, NH, USA) were being prepared to desired concentration daily prior to use. Cotton role was used to prepare the mini column with the dimension of $25 \times 4 \text{ mm}$

(length \times inner diameter). All solvents and reagents were of highest available purity and at least of analytical grade, in which the presence of REEs and U were not detected.

Mini column preparation

Thirty milligrams of quinalizarin was dissolved in dimethyl sulfoxide (DMSO) and the cotton roll was dyed in prepared solution on heater at temperature of $100 \text{ }^\circ\text{C}$ for at least 4 h. Then, it was washed by cold distilled water and dried in an oven. This procedure leads the quinalizarin to be fixed on cotton and the reproducibility of procedure to be guaranteed. This cotton roll was replaced in a sector of an empty cylindrical tube. Finally, the column was connected with polytetrafluoroethylene (PTFE) tubing to a peristaltic pump and rotary valve to form the pre-concentration system.

On-line pre-concentration procedure

The schematic of integrated extraction/elution set up is shown in Figure 1.

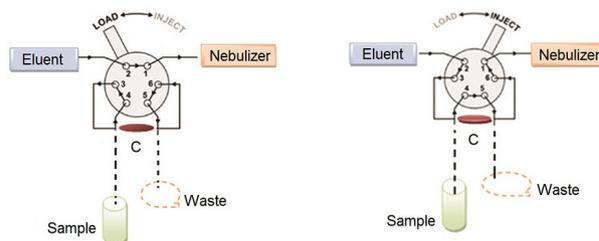


Figure 1. Schematic set up of on-line pre-concentration/determination of desired elements for load and inject process. C: Mini column.

Before loading the mini column, it was conditioned for pre-concentration with buffer solution (ammonium acetate 0.1 mol L^{-1}) adjusted to pH 7 by 0.1 mol L^{-1} of hydrochloric acid or sodium hydroxide. For extraction procedure, 25 mL of aqueous sample solution ($100 \mu\text{g L}^{-1}$) of REEs and U (adjusted to desired pH) was loaded on prepared mini column at flow rate of 2 mL min^{-1} with peristaltic pump and rotary valve in load position.

Injection step

After loading time, the valve was switched to elution position. The retained REEs and U on the cotton roll were eluted with nitric acid (2 mol L^{-1}) and were directly introduced to the nebulizer. All the measurements were done as peak height of emission signal. After analyte determination, the injection valve was switched back to loading position and tubing lines were washed by distilled water to eliminate remaining acid.

Result and Discussion

In order to optimize the extraction and pre-concentration conditions, some experimental variables were evaluated and optimized using one at a time approach. Type of eluent and pH were optimized in our off-line previous work.³⁷ Sample flow rate, eluent flow rate, breakthrough volume and interfering elements were studied and optimized in this survey. The optimum instrumental conditions for ICP OES were done by experimental design based on Box-Behnken model. Selected analytical wavelength of REEs and U could be seen in the Supplementary Information (Table S1).

ICP OES optimization parameters

Box-Behnken experimental design was applied to optimize the operating parameters to obtain better sensitivity. The Box-Behnken design (BBD) is an independent quadratic design that does not contain any points at the vertices of the experiment region. The radio frequency of ICP OES (plasma power), nebulizer gas flow rate, sample uptake rate and viewing height were selected as independent variables. Signal to background ratio (SBR) values of REEs were studied as response. Independent variables values are shown in table 1 and the BBD design could be seen in the Supplementary Information (Table S2).

Table 1. Independent variable values

Variable	-	Center point	+
Viewing height / mm	9	12	15
Radio frequency (RF, plasma power) / kW	1	1.25	1.5
Nebulizer gas flow rate / (L min ⁻¹)	0.6	0.8	1
Sample uptake rate / (mL min ⁻¹)	1	2	3

According to the design, each variable was studied at least in 2 levels. The central point was made in 5 replicates adding up to 29 experiments. The experimental data were processed by Design-Expert software version 7.0.⁴⁰ All measurements were carried out using a test solution with 1 mg L⁻¹ of La, Nd and Yb. Response was obtained for geometric mean of results by plotting the mean SBR against radio frequency (RF, plasma power), nebulizer gas flow rate, viewing height and sample uptake rate.

Based on the analysis of variance (ANOVA) results (Table 2), the *p*-values of these parameters, A = Rf, B = nebulizer flow, C = viewing height, D = sample uptake rate, AB, BC, A², B², D², AB², B²C, B²D, are less than 0.050 and could be named as significant parameters. Furthermore, the values of different R², coefficient of variation, standard

deviation and adequate precision, indicated the significance and reliability of the model.

Table 2. Analysis of variance of response

Parameter	Value	Parameter	Value
Standard deviation	0.021	R-squared	0.9928
Mean	0.62	adjusted R-squared	0.9857
Coefficient of variation / %	3.41	predicted R-squared	0.8757
Press	0.11	adequate precision	41.367

3D response surface plots of AB and BC terms are demonstrated in Figures 2 and 3. Maximum area are clear in the figures (red area).

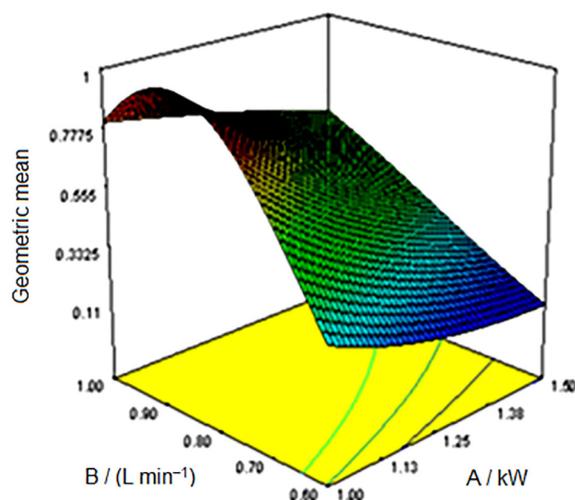


Figure 2. 3D Response surface plots of AB terms. A: Radio frequency (RF) power generator; B: nebulizer flow rate.

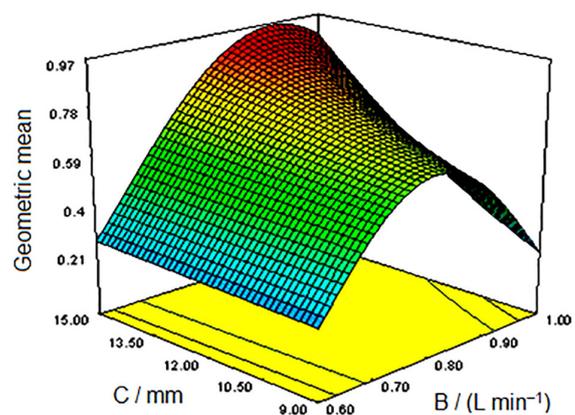


Figure 3. 3D Response surface plots of BC terms. B: Nebulizer flow rate; C: viewing height.

Plot based, the optimal conditions of selected factors were attained. So, the RF (plasma power) of 1 kW, viewing height of 15 mm and nebulizer gas flow rate of 0.9 L min⁻¹ were used for instrument parameter analysis.

Effect of sample flow rate

In an analytical procedure, analysis time is of great attention. As the sample flow rate through mini columns is one of the steps that controls this time, so this parameter was investigated between 1.3 and 6.6 mL min⁻¹. According to obtained results (Figure 4), optimal flow rates were in the range 1.3-2 mL min⁻¹. It was assumed that this pre-concentration is kinetic dependent.

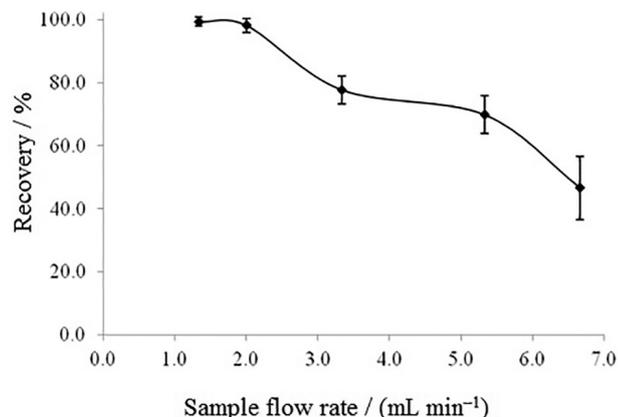


Figure 4. Effect of sample flow rate on the extraction efficiency. Pre-concentration conditions: 25 mL of 100 µg L⁻¹ of analytes; pH 7; eluent: HNO₃ 2 mol L⁻¹ with flow rate of 3 mL min⁻¹.

Effect of concentration and flow rate of eluent

REEs and U desorption were studied by increasing the acid concentration from 0.1 up to 3 mol L⁻¹. Results were judged based on recovery values. Total desorption was attained at concentration above 1 mol L⁻¹. In order to get a guaranteed elution, 2 mol L⁻¹ nitric acid solution was chosen as optimum eluent concentration. Also, the influence of eluent flow rate on cations desorption was examined. This modification was done in the range from 0.6-6.6 mL min⁻¹. Elution flow rate was evaluated in off-line mode first (2 mL eluent was passed through mini column in different rate). Different rates did not show any differences in emission signals. After that, in on-line mode, results showed that analytical signal of desorbed analytes increased as flow rate increased up to 1.4 to 4.7 mL min⁻¹ due to peak narrowing and maximum signal to noise (Figure 5). Improper sample introduction at upper flow rate caused decreasing emission signal.

Interference studies

The effect of interfering ions on the recovery of REEs and U up to tolerance level (90%) was studied on 5 µg L⁻¹ of desired analytes under the corresponding optimum

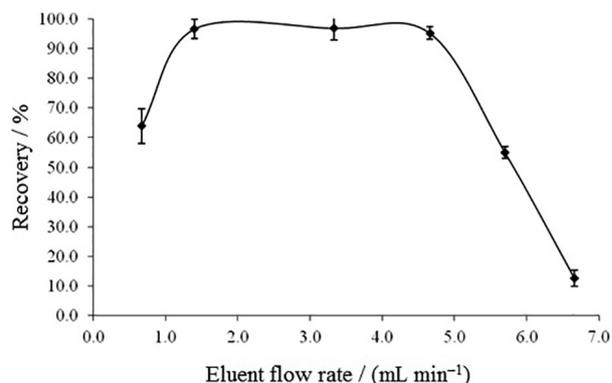


Figure 5. Effect of eluent flow rate on the extraction efficiency. Pre-concentration conditions: 25 mL of 100 µg L⁻¹ of analytes; pH 7; eluent: HNO₃ 2 mol L⁻¹.

pre-concentration conditions. A number of common anions such as Cl⁻, Br⁻, C, P, and S were examined up to 100 µg mL⁻¹ and no interferences were found. The effect of some base metal cations such as Cu^{II}, Cd^{II}, Co^{II}, Ti^{II}, Cr^{VI}, Mn^{II}, Fe^{II}, Zn^{II} and Ni^{II}, usually found in water samples, was studied in the range of 1000-5000 folds of desired analyte. The results showed there was not any serious interference on recovery of target analytes. Among alkaline and alkaline earth metal ions (Na⁺, K⁺, Ca²⁺, Mg²⁺), quinalizarin form stable complex with Mg²⁺. It seems that quinalizarin form more stable complexes with REEs and U than Mg²⁺ at pH 7, so no interferences from these common ions were observed in the range of 5000 folds of desired analytes.

Analytical performance

The dependence of REEs and U recoveries on the volume of real sample was evaluated using 25-400 mL of sample solution containing 1.0 µg of desired elements. The breakthrough volumes of 16 elements were 400 mL for various ions (Table 3). The calibration graphs with optimized conditions were obtained using 25 mL of multi elements standard solutions in the range of 0.3-30 µg L⁻¹. Calibration curves were plotted as emission intensity of extracted analytes against their initial concentration in aqueous phase. Precision of method was evaluated using 5 portions of standard solution of 5 µg L⁻¹. The figure of merits of proposed method is summarized in table 3. The obtained RSD% values were lower than 6%, except for Sm and U. The enhancement factors (EF) of analytes were calculated as the respect of the slope of calibration curve after pre-concentration to that obtained by direct injection of standard solution of desired elements.

A comparison with the analytical performance of proposed method and some of the published pre-concentration methods for REEs elements were summarized

Table 3. Figures of merit of the proposed method

Element	Enhancement factor ^a	LOD / ($\mu\text{g L}^{-1}$)	Calibration equation ^a	Linear range / ($\mu\text{g L}^{-1}$)	Correlation coefficient	Breakthrough volume / mL	RSD ^b / %
Y	60.7	0.005	$y = 970.85x - 152.91$	0.3-10	0.9961	400	4
La	58.5	0.002	$y = 250.3x - 87.4$	0.3-10	0.9952	400	5
Ce	46.2	0.130	$y = 89.13x - 3.64$	0.3-10	0.9996	400	3
Pr	45.7	0.301	$y = 66.32x + 3.37$	0.3-10	0.9980	400	4
Nd	40.4	0.077	$y = 44.39x + 24.39$	0.3-10	0.9970	400	4
Sm	35.8	0.171	$y = 60.83x + 0.27$	0.3-10	0.9986	400	16
Eu	25.4	0.028	$y = 941.3x + 78.02$	0.3-5	0.9980	400	5
Gd	53.9	0.024	$y = 258.36x + 16.25$	0.3-10	0.9997	400	6
Tb	51.1	0.286	$y = 100.73x + 27.65$	0.3-10	0.9992	400	5
Dy	40.4	0.120	$y = 119.97x + 10.38$	0.3-10	0.9998	400	3
Ho	44.5	0.011	$y = 95.6x + 0.76$	0.3-10	0.9990	400	3
Er	51.8	0.022	$y = 178.1x + 2.79$	0.3-10	0.9990	400	4
Tm	49.2	0.145	$y = 362.92x + 37.08$	0.3-10	0.9998	400	3
Yb	63.9	0.023	$y = 1278.3x - 224.83$	0.3-10	0.9964	400	3
Lu	66.7	0.005	$y = 568.59x - 7.57$	0.3-10	0.9998	400	3
U	11.6	0.420	$y = 14.53x - 0.75$	1.0-30	0.9989	400	22

^aObtained by 25 mL solution; ^brelative standard deviation for $n = 5$ replicate measurements at $5 \mu\text{g L}^{-1}$. LOD: Limit of detection.

Table 4. Comparison of the proposed method and some of the published pre-concentration methods for rare earth elements (REEs)

Element	Technique	LOD / (ng mL^{-1})	RSD / %	Reference
Pr, Sm, Eu, Gd, Ho, Tb, Tm, Yb, Lu, Dy	SPE-ICP OES	0.01-0.42	–	25
REE	CPE-ICP OES	0.041-0.045	1-6	28
Eu, Gd, Ho, La, Tb, Yb, Sm	MWCNT-ICP OES	3-57	< 6	11
REE	magnetic-SPE-ICP-MS	0.0004-0.0014	2-7	16
La, Sm, Nd	SPE-ICP OES	3.9-7.4	< 3	32
REE	on-line-SPE-ICP-MS	0.0004-0.0025	< 8	19
REE	MWCNT-ICP-MS	0.0001-0.0016	–	18
Ce, Dy, La, Sm, Y, U	on-line-SPE-ICP OES	0.011-0.069	1-8	24
REE, U	on-line-SPE-ICP OES	0.002-0.420	3-6, ^a 22 ^b	this study

^aREE; ^bU. CPE: Cloud point extraction; ICP OES: inductively coupled plasma optical emission spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; MWCNT: multi walled carbon nanotube; SPE: solid phase extraction.

in Table 4. It is obvious that this methodology is comparable with other method and in some cases better LODs and precision.

Analysis of real sample

Certified natural water reference materials are not available for REEs and U.⁴¹ Thus, the developed method was applied to the pre-concentration and determination of spiked REEs and U in lake, well and tap water. All water samples were collected in polyethylene bottles and acidified up to $\text{pH} = 2$ in order to ion metals do not be adsorbed by

wall of bottles. Aqueous standard solutions along blank (25 mL deionized water adjusted pH to 7 by ammonium acetate solution) without matrix optimization were used for calibration and determination of desired elements in samples. The obtained results are presented in Table 5. The Student's t -test showed that each mini column supports 20 pre-concentration cycles (data are not shown).

As can be seen, for matrix with high major elements concentration (high TDS, Urumieh Lake, Lorestan Well, Table 6), recoveries have been decreased. For routine analysis correction factor or calibration standard solutions with optimized matrix is applicable.

Table 5. Results of rare earth elements (REEs) and uranium (U) determination in natural water samples

Element	Urumieh Lake			Lorestan Well			Tap water Karaj		
	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	Recovery / %	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	Recovery / %	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	Recovery / %
Y	20.0	3.3	16	5.0	3.6	73	5.0	5.0	100
La	20.0	13.4	67	5.0	3.4	68	5.0	4.9	98
Ce	20.0	13.9	70	5.0	3.5	70	5.0	4.5	91
Pr	20.0	14.9	75	5.0	3.3	67	5.0	4.6	92
Nd	20.0	14.7	74	5.0	3.9	79	5.0	4.7	94
Sm	20.0	15.1	76	5.0	4.0	80	5.0	4.9	98
Eu	20.0	4.3	22	5.0	4.7	94	5.0	4.8	97
Gd	20.0	14.4	72	5.0	4.0	80	5.0	4.9	98
Tb	20.0	14.3	72	5.0	3.9	77	5.0	5.0	100
Dy	20.0	14.8	74	5.0	3.4	69	5.0	5.1	102
Ho	20.0	14.9	75	5.0	3.8	76	5.0	5.2	105
Er	20.0	15.0	75	5.0	3.9	78	5.0	5.0	100
Tm	20.0	15.0	75	5.0	4.1	81	5.0	5.5	111
Yb	20.0	3.6	18	5.0	4.9	89	5.0	4.7	93
Lu	20.0	14.7	74	5.0	4.1	83	5.0	5.0	100
U	20.0	26.6	133	5.0	5.6	112	5.0	2.8	56

Table 6. Urumieh and Lorestan matrix elements^a

Major element	Urumieh / ($\mu\text{g mL}^{-1}$)	Lorestan / ($\mu\text{g mL}^{-1}$)
Ca	175.0	10.0
Na	80.0	5.0
K	7.5	0.5
Mg	70.0	10.0

^aAnalysed in the Applied Geological Research Center of Iran.

This method was applied for REEs and U determination in two carbonate mineral samples from central Iran zone (Tabas) too. An aliquot of pulverized sample (0.5 g) was digested with aqua regia (HCl:HNO₃, 3:1) for 2 h at 95 °C. The sample was cooled and then diluted up to 50 mL with deionized water. Digested sample with adjusted pH was loaded on mini column in optimized flow rate, and then the adsorbed REEs and U were eluted and analyzed by ICP OES. Recoveries are presented in Table 7.

REEs in some samples were not detected directly by ICP OES. So, 2 $\mu\text{g L}^{-1}$ of REEs and U standard solution was

Table 7. Determination of rare earth elements (REEs) ions in carbonate minerals

Element	Carbonate sample K 29			Carbonate sample K 65		
	Found directly by ICP OES ^a / ($\mu\text{g g}^{-1}$)	Proposed method / ($\mu\text{g g}^{-1}$)	Recovery / %	Found directly by ICP OES / ($\mu\text{g g}^{-1}$)	Proposed method / ($\mu\text{g g}^{-1}$)	Recovery / %
Y	0.6	0.7	114	7.5	5.5	73
La	1.36	0.9	63	8	7.8	98
Ce	< LOD	1.8	–	15	14.5	97
Pr	< LOD	0.5	–	< LOD	2.8	–
Nd	< LOD	1.3	–	6.2	6.5	105
Sm	< LOD	0.3	–	< LOD	2.0	–
Eu	< LOD	0.4	–	< LOD	1.51	–
Gd	< LOD	0.6	–	< LOD	2.7	–
Tb	< LOD	0.4	–	< LOD	1.1	–
Ho	< LOD	0.4	–	< LOD	0.7	–
Dy	< LOD	0.3	–	< LOD	1.6	–
Er	0.6	0.5	84	1.9	1.8	96
Tm	< LOD	0.4	–	< LOD	1.2	–
Yb	0.4	0.4	95	1.1	1.2	113
Lu	< LOD	0.4	–	< LOD	1.2	–
U	6.8	3.2	48	8.91	7.3	82

^aICP OES: Inductively coupled plasma optical emission spectrometry. K29, K65: code of carbonate minerals from central Iran zone.

Table 8. Results of some rare earth elements (REEs) in digested sample by add-found method

Carbonate sample K 29				
Element	Present in the solution of digested sample before loading ^a / ($\mu\text{g L}^{-1}$)	Added to digested solution / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	Recovery / %
Ce	3.5	2	6.5	118
Pr	0.9	2	3.6	122
Nd	1.2	2	5.0	155
Sm	0.5	2	3.4	134
Eu	0.8	2	4.8	166
Gd	1.1	2	4.1	130
Tb	0.9	2	3.0	103
Ho	0.7	2	3.3	120
Dy	0.6	2	3.6	139
Er	1.2	2	3.9	119
Tb	0.9	2	3.0	103
Tm	0.7	2	3.8	143
Carbonate sample K 65				
Element	Present in the solution of digested sample before loading ^a / ($\mu\text{g L}^{-1}$)	Added to digested solution / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	Recovery / %
Pr	5.6	2	8.2	107
Sm	4.06	2	5.8	95.7
Eu	3.02	2	4.53	90.1
Gd	5.46	2	7.53	100.9
Tb	2.1	2	3.02	73.2
Ho	1.37	2	2.45	72.7
Dy	3.2	2	4.8	90.7
Tm	1.56	2	2.7	75.8
Lu	2.4	2	3.83	86.9

^a10 mL of digested sample diluted to 50 mL (concentrations obtained by proposed method). K 29, K 65: code of carbonate minerals from central Iran zone.

added to the solution of digested sample. The recoveries are demonstrated in Table 8.

Conclusions

The proposed on-line solid phase extraction pre-concentration methodology using a mini column filled with green sorbent based on dyed cotton roll by quinalizarin is a simple way suitable for determination of 14 REEs and uranium simultaneously in real samples. The procedure offers acceptable accuracy, precision and significant enrichment factor. In addition, this procedure is very straightforward, environment friendly and economical since only quinalizarin without any modification was used for REEs and U pre-concentration simultaneously. This method has feasibility for automation. In this procedure extraction, pre-concentration and elution steps are integrated. The results of real samples analysis showed a strong performance for this method for pre-concentration/determination of the analytes from real aqueous samples and carbonate minerals.

Supplementary Information

Supplementary data are available free of charge at <http://jbc.sbg.org.br> as PDF file.

Acknowledgments

The authors of this survey would like to thank the Environmental Chemistry and Green Technology Department of Chemistry and Chemical Engineering Research Center of Iran and ICP OES laboratory in applied geology research center of geological survey of Iran.

References

1. Murakami, M.; Hamanaka, E.; Takada, T.; *Anal. Lett.* **2005**, *38*, 2449.
2. U.S. Geological Survey (USGS); *Rare Earth Elements-Critical Research for High Technology*, Fact Sheet 087-02, USGS: Virginia, 2002.

3. Gob, S.; Lodes, A.; Nolde, N.; Bau, M.; Jaccob, D. E.; Markl, G.; *Appl. Geochem.* **2013**, *33*, 127.
4. Moldoveana, G. A.; Papangelakis, V. G.; *Hydrometallurgy* **2012**, *117*, 71.
5. Hu, W.; Noreus, D.; *J. Alloys Compd.* **2003**, *356*, 734.
6. Gschneidner, K. A.; Pecharsky, V. K.; *J. Rare Earths* **2007**, *24*, 641.
7. Guanming, Q.; Xikun, L.; Tai, Q.; Haitu, Z.; Honghau, Y.; Rutting, M.; *J. Rare Earths* **2007**, *25*, 281.
8. Zhang, Z.; Sun, Q.; Ding, S.; Liang, T.; Zhang, Ch.; Yan, J.; *Biol. Trace Elem. Res.* **2005**, *107*, 73.
9. Anitha, S.; Challarj, E. S. E.; Saranraj, P.; *J. Ecobiotechnol.* **2010**, *217*, 01.
10. Lijun, W.; Tao, L.; Aitang, H.; Shiming, D.; Chaosheng, Z.; Xin, Y.; *J. Rare Earths* **2005**, *23*, 747.
11. Liang, P.; Liu, Y.; Guo, L.; *Spectrochim. Acta, Part B* **2005**, *60*, 125.
12. Hakim, L.; Sabarudin, A.; Oshima, M.; Motomizo, S.; *Anal. Chim. Acta* **2007**, *588*, 73.
13. Nobuo, S.; Naoki, K.; Hiroshi, I.; *Appl. Geochem.* **2008**, *23*, 2955.
14. Dick, D.; Wegner, A.; Gabrielli, P.; Ruth, U.; Barbante, C.; Kriews, M.; *Anal. Chim. Acta* **2008**, *621*, 140.
15. Chung, C. H.; Brenner, I.; You, C. F.; *Spectrochim. Acta, Part B* **2009**, *64*, 849.
16. Su, S.; Chen, B.; He, M.; Hu, B.; Xiao, Z.; *Talanta* **2014**, *119*, 458.
17. Wen, B.; Shan, X. Q.; Xu, S. G.; *Analyst (Cambridge, U. K.)* **1999**, *124*, 621.
18. Cho, J.; Chung, K. W.; Coi, M. S.; Kim, H. J.; *Talanta* **2012**, *99*, 369.
19. Hirata, S.; Kajia, T.; Aihara, M.; Honda, K.; Shikino, D.; *Talanta* **2002**, *58*, 1185.
20. Maquieira, A.; Elmahdi, H.; Puchades, R.; *J. Anal. At. Spectrom.* **1999**, *11*, 99.
21. Rao, T. P.; Kala, R.; *Talanta* **2004**, *63*, 949.
22. Karadaş, C.; Kara, D.; Fisher, A.; *Anal. Chim. Acta* **2011**, *689*, 184.
23. Huang, C. Z.; Jiang, Z.; Hu, B.; *Talanta* **2007**, *73*, 274.
24. Bahramifar, N.; Yamini, Y.; *Anal. Chim. Acta* **2005**, *540*, 325.
25. Karadas, C.; Kara, D.; *Water, Air, Soil pollut.* **2014**, *225*, 2192.
26. Chandrasekaran, K.; Karunasagar, D.; Arunachalam, J.; *J. Chromatogr. A* **2008**, *118*, 59.
27. Taicheng, D.; Tiny, C. H.; Xianjin, Z.; *J. Anal. At. Spectrom.* **2002**, *17*, 410.
28. Li, Y.; Hu, B.; *J. Hazard. Mater.* **2010**, *174*, 534.
29. Hang, C. Z.; Hu, B.; Jiang, Z. C.; Zhang, N.; *Talanta* **2007**, *71*, 1239.
30. Praveen, R. S.; Daniel, S.; Rao, T. P.; Sampath, S.; Rao, K. S.; *Talanta* **2006**, *70*, 437.
31. Dave, S. R.; Kaur, H.; Menon, S. K.; *React. Funct. Polym.* **2010**, *70*, 692.
32. Chen, S.; Xiao, M.; Lu, D.; Zhan, X.; *Anal. Lett.* **2007**, *40*, 2105.
33. Zeren, F.; Yilmaz, V.; Arslan, Z.; *Microchem. J.* **2013**, *110*, 178.
34. Shariati, S.; Yamini, Y.; Faraji, M.; Saleh, A.; *Microchim. Acta* **2009**, *165*, 65.
35. Zanjanchi, M. A.; Noei, H.; Moghimi, M.; *Talanta* **2006**, *70*, 933.
36. Cozza, G.; Mazzorana, M.; Papinutto, E.; *Biochem. J.* **2009**, *421*, 387.
37. Hassan, J.; Zari, N.; Tabar-Heydar, K.; *J. Anal. Chem.* **2016**, *71*, 36.
38. Borokowski, J. J.; *Technometrics* **1995**, *37*, 399.
39. Anderson, S. S.; dos Santos, W. N. L.; Ferreira, S. L. C.; *Spectrochim. Acta, Part B* **2005**, *60*, 737.
40. Stat-Ease, Inc; *Design Expert Software Version 7.0*; Minneapolis, USA, 2006.
41. Jarvis, K. K.; Gay, A. L.; Houk, R. S.; *Handbook of Inductively Coupled Plasma Mass Spectrometry*; Springer: Berlin, 1992.

Submitted: February 18, 2016

Published online: March 14, 2016