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## Selective micro extraction of rare earth elements and yttrium in rock samples using silica modified with xylenol orange and their determination by ICP-AES

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### Abstract

A systematic study on the selective extraction of rare earth elements (REEs) and yttrium onto silica modified with xylenol orange (SMXO) was carried out and a scheme for the pre-concentration and separation of REEs and Y in rock samples is discussed. A simple single step preparation of silica and its modification by xylenol orange in presence of cetyltri-methylammonium bromide is enumerated. Characterisation of prepared adsorbent was carried out by surface area analysis, IR data and SEM data. REEs and Y were adsorbed onto SMXO at  $\text{pH} \geq 3$  and after a contact period of 30 minutes. Adsorbed REEs and Y were eluted from SMXO with 0.5% (w/v) EDTA solution. Aluminium and iron when present above 200 mg/L were interfering in the analysis of REEs. Aluminium interference was eliminated by removing it as sodium aluminate in the fusion stage of rock samples. Interference of  $\text{Fe}^{3+}$  was avoided by reducing Fe (III) to Fe (II) using hydroxylamine hydrochloride. Separated REEs were determined by ICP-AES. The proposed method is simple, accurate and the precision is characterized by the % RSD ranges from 2.0-5.1% at the determination limit ranging from 0.2-5 $\mu\text{g/mL}$ .

**Keywords:** Rare earth elements, rock samples, preconcentration, silica modified with xylenol orange, ICP-AES

### Introduction

Rare earth elements (REEs) form a coherent group of elements of geochemical significance and their chondrite distribution pattern in rock sample is important in petro-genetic studies<sup>[1]</sup>. Hence, information concerning REE concentration and their relative distribution in soil and rock are very important for geo-chemical interpretation. The crustal abundance of most of the REEs is low and of the order of microgram per gram<sup>[1, 2]</sup>.

ICP-AES is the commonly used technique for the determination of rare earth elements due to its good sensitivity and simplicity<sup>[3, 4]</sup>. Despite its advantages, the determination of rare earth elements by ICP-AES in rock sample is difficult due to the spectral interference caused by major elements of the rock<sup>[5]</sup>. Therefore, it is necessary to pre-concentrate and separate REEs from major elements prior to their determination by ICP-AES.

Techniques used for routine separation and pre-concentration of REEs in geological samples are co-precipitation<sup>[6, 7]</sup>, ion-exchange<sup>[8, 9]</sup> and solvent extraction<sup>[10, 11]</sup>. However, these procedures possess the disadvantages like use of carcinogenic organic compounds, difficulty in phase separation, lower sample throughput and low pre-concentration factor<sup>[12]</sup>. Presently solid phase extraction (SPE) methods are preferred over these methods due to its advantages like, high enrichment factor, high sample through put, fast kinetics, rapid phase separation and low cost<sup>[13]</sup>. Among many types of solid phases employed in SPE, silica gel immobilised with chelating agents have received wide acceptance due to its non- swelling properties, ease of modification, large specific surface area, fast kinetics, good mechanical and thermal stability<sup>[14]</sup>.

Selectivity of the solid phase adsorbents for trace elements can be improved by modifying the solid substrate with reagent which form complex with trace elements<sup>[15]</sup>. Authors in our previous study have prepared the adsorbent silica modified xylenol orange and used it for the preconcentration and determination of uranium in hydro geochemical samples and sea water<sup>[16]</sup>. Xylenol orange is a chromogenic reagent and which is known to form complexes with REEs also<sup>[17, 18]</sup>. Hence a study was undertaken to utilize this adsorbent for the preconcentration of REEs in rock samples.

## Experimental

A Jobin Yvon model 2000(2) sequential ICP-AES from M/S Jobin Yvon, France was used for the determination rare earth elements. The instrumental parameters used are given in Table-1. The spectral lines used in the study, are given in Table-2.

**Table 1:** Operating parameters of ICP-AES system.

RF Generator	40.68 MHz (crystal controlled)
Forward power	1000 W
Reflected power	<5 W
Gas flow	12 lit min <sup>-1</sup> coolant
Monochromator	Modified Czerny-Turner
Focal Length	640 mm
Diffraction grating	4320 grooves mm <sup>-1</sup>
Wavelength range	170-440 nm
Nebulizer	Concentric
Solution uptake rate	1.0 ml min <sup>-1</sup>
Slits	21 $\mu$ m entrance, and 22 $\mu$ m exit
Detector	Photomultipliers R-106
Observation height	11 mm above load coil

**Table 2:** Spectral lines used for emission measurement of REEs and Y

Element	Wavelength (nm)	Element	Wavelength (nm)
La	398.852	Dy	353.170
Ce	418.660	Ho	345.600
Pr	422.293	Er	349.910
Nd	430.358	Tm	346.220
Sm	442.434	Yb	328.937
Eu	381.967	Lu	261.542
Gd	342.247	Y	371.030
Tb	350.917		

The pH measurement was carried out by using an Indian make Elico, Digital pH meter, Model LI-122.

## Reagents

All reagents and chemicals used were of analytical-reagent grade and type 1 water was utilized throughout the experiment.

Preparation of rare earth standard solutions:

The REE stock solution of 1000  $\mu$ g mL<sup>-1</sup> was prepared from high purity oxides (99.99 or 99.999%), Johnson Matthey, Royston, U.K and suitable working standard solutions were prepared by dilution.

Sodium metasilicate Na<sub>2</sub>SiO<sub>3</sub>. 5 H<sub>2</sub>O (Merck GR)– 0.3M solution of sodium meta silicate is prepared by dissolving 30g of sodium meta silicate in 500 mL water.

Cetyltrimethylammonium bromide (CTAB) (Rolet, India): 0.1% (w/v) solution in water.

Xylenol Orange: (XO) (Merck GR): 0.1% (w/v) solution in water.

Ethylenediaminetetraacetic acid solution (EDTA) (Merck GR): 0.5% (w/v) solution in water.

Ascorbic acid (SD Fine AR): 5% (w/v) solution in water.

## Synthesis of silica modified with xylenol orange (SMXO)<sup>[16]</sup>

500 mL 0.3 M sodium metasilicate solution was taken in a 1 litre beaker. This solution was mixed with 25 mL 0.1% (w/v) Cetyltrimethylammonium bromide and 25 mL of 0.1% (w/v) xylenol orange. 30 mL of 50% (v/v) HCl was added with continuous stirring and solution was kept undisturbed overnight. Gel formed was filtered and washed

thoroughly to remove un-adsorbed reagent. The adsorbent formed was dried in an air oven at 80° C. It was ground in an agate mortar and stored in plastic vial.

## Characterisation of adsorbent

Specific surface area and pore size distribution of adsorbent was determined by Adsorption – desorption experiments using nitrogen and were carried out at 77°K on NOVA 1000 Surface area analyser; Quantachrome Corporation, U.S.A. Nicolet Avatar 300 Result is given in Table-3. FT-IR spectrometer has been used to characterize SMXO using KBr pressed disk techniques. Results are given in fig-1. SEM data of the synthesized material was investigated with FEI Quanta 400 ESEM microscope. Results are given in fig-2.

## Optimisation of parameters for pre-concentration REEs using SMXO

Experiments were carried out to optimise pH, equilibration time and amount of adsorbent required for adsorption of REEs onto SMXO. The conditions for desorption of REEs from SMXO were also optimised using batch experiments. 25  $\mu$ g each of individual REEs were taken in 100 mL beakers and pH of the solutions were adjusted to 1-10 and kept in contact with 0.01g - 0.5g of SMXO for time durations of 5 minutes to 2 hours. The solutions were filtered and the un-adsorbed REEs in the filtrate were determined by Inductively Coupled Plasma Atomic emission spectrometry. The results are given in Fig 3, 5& 6. Desorption of REEs from the adsorbent was carried out using different concentrations of acids and complexing reagents like, EDTA, oxalic acid and ammonium oxalate. Recovered REEs in the leach solutions were determined ICP-AES. The results are shown in Fig-7.

## Sorption capacity of SMXO for different rare earth element

Batch experiments were performed to calculate the sorption capacity of the adsorbent for REEs. Different volumes of standard solutions ranging from 0.5 to 5 ml of 1 mg mL<sup>-1</sup> of respective REEs were taken in beakers. pH of the solutions were adjusted to 3 and kept in contact with 50mg of the adsorbent for 30 minutes and filtered. REE concentrations in the filtrate were analysed using ICP-AES.

## Effect of major elements on the adsorption of REEs to SMXO.

Experiments were carried out to find the effect of major elements of rock like aluminum, iron, calcium, magnesium, manganese, sodium and potassium on the pre-concentration of REEs using SMXO. 100 mL water was doped with 50  $\mu$ g each of REEs and 200  $\mu$ g, 400  $\mu$ g, 500  $\mu$ g, 1 mg and 2 mg of different major elements. pH of the solutions was adjusted to 3 and kept in contact with 50 mg of the adsorbent for 30 minutes. The adsorbent was filtered and washed thoroughly with water. REEs adsorbed on SMXO were recovered with 10 mL 0.5% EDTA solution and made up to 25 mL. Recovered REEs were estimated using ICP-AES.

## Recommended procedure for the determination of REEs in rock samples

0.5g of rock sample was fused with 3g sodium hydroxide in a nickel crucible. Contents of the crucible were transferred into 100 mL of water in 500 mL beaker. The solution was

boiled and filtered. The residue was dissolved in 100 mL 3% (v/v) HCl. 10 mL of 5% (w/v) hydroxylamine hydrochloride was added to it. pH of the solution was adjusted to 3 with  $\text{NH}_4\text{OH}$  and HCl. The solution was kept in contact with 50 mg of SMXO for 30 minutes. Solution was filtered and the adsorbent was washed thoroughly with water to remove all the unadsorbed elements. Adsorbed REEs were eluted from SMXO with 10 mL of 0.5 % (w/v) EDTA solution and made up to 25 mL. The recovered REEs were estimated by ICP-AES.

## Results and discussion

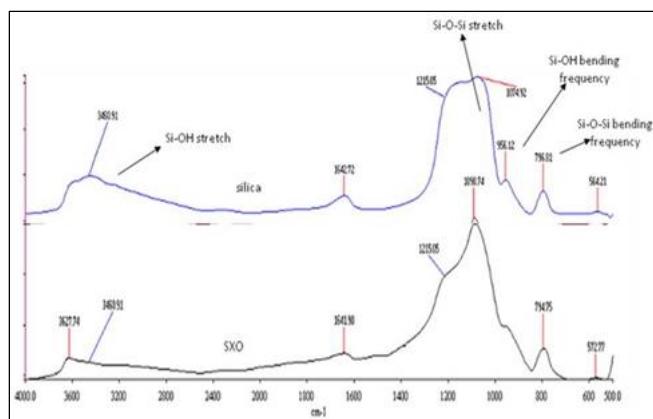
The reagent xylenol orange was chosen for immobilisation on silica due to its high chelating tendency for rare earth elements. Silica modified with xylenol orange was synthesised using a novel procedure. The suggested method of synthesising SMXO is a single step process. Synthesis of silica from sodium silicate solution and its modification by xylenol orange in presence of CTAB takes place simultaneously. It was observed that in the absence of surfactant, xylenol orange was completely removed from the silica surface during washing. The surfactant CTAB acts as a bridge between silica gel and xylenol orange molecule. SMXO synthesized by this procedure has better stability over the adsorbent prepared by coating silica gel with reagent in presence of CTAB.

The specific surface area, pore volume and pore diameter of unmodified silica and SMXO have been obtained from BET and BJH calculations. The results obtained are given in table 3. There is a drastic reduction in surface area of SMXO compared to silica. This can be ascribed due to the exchange of most of the active sites of the silica by XO species. The decrease in pore volume and pore diameter of SMXO compared to silica also points to the fact that most of the pores in silica were blocked by XO for nitrogen adsorption.

**Table 3:** Surface area, pore volume and pore diameter of silica and SXO

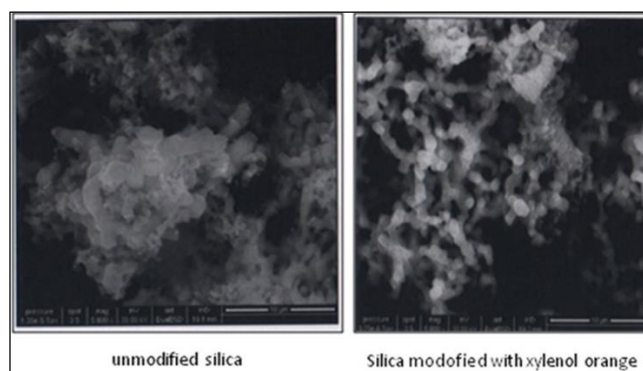
Material	Specific surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Average pore diameter ( $\text{\AA}$ )
Silica	88.64	0.1674	75.75
SXO	22.6084	0.03482	60.606

IR data of silica and SMXO are shown in fig 1. Peak at  $3460\text{ cm}^{-1}$  corresponds to Si-OH stretching frequency,  $1642\text{ cm}^{-1}$  corresponds to O-H stretching frequency,  $1080\text{ cm}^{-1}$  corresponds to Si-O-Si stretching frequency,  $956\text{ cm}^{-1}$  corresponds to Si-OH bending frequency and  $795\text{ cm}^{-1}$  corresponds to Si-O-Si bending frequency<sup>[19]</sup>. It was noticed from the IR spectrum of the SMXO that Si-OH groups present on silica was reduced in comparison with the parent silica. It was reported that all modified silica exhibit a clear cut decrease in silanol group as compared to silica<sup>[20]</sup>. This was inferred from the decrease in peak height of Si-OH stretching frequency at  $3460\text{ cm}^{-1}$  and Si-OH bending frequency at  $956\text{ cm}^{-1}$ . Also it was noticed from two spectra that peak area of Si-O-Si peak decrease after modification. These two factors suggest that XO was grafted to silica by the removal of hydroxyl group.



**Fig 1:** IR spectrum of silica and SXO

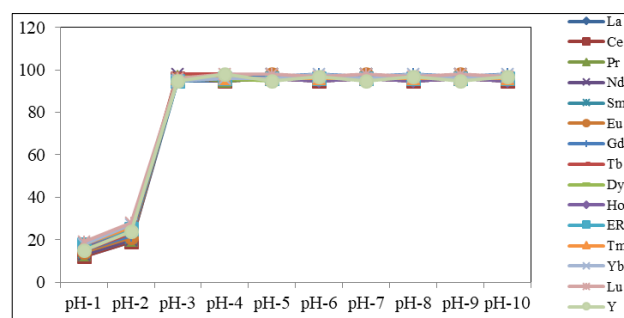
Morphology of silica and SMXO obtained from SEM data is given in fig2. This picture shows clear morphological difference between silica and modified sample which support surface modification.



**Fig 2:** SEM data of silica and SXO

## Adsorption of REEs on to SMXO

Result of adsorption of REEs and Y on to SMXO at different pHs is given in the fig-3. Quantitative adsorption of REEs to SMXO is observed at  $\text{pH} \geq 3$ .



**Fig 3:** Variation of adsorption with pH of solution

REEs are adsorbed onto SMXO due to the formation of REE- xylenol orange complex on the adsorbent SMXO. Xylenol orange forms 1:1 complexes with REEs (fig 4b)<sup>[21]</sup>.

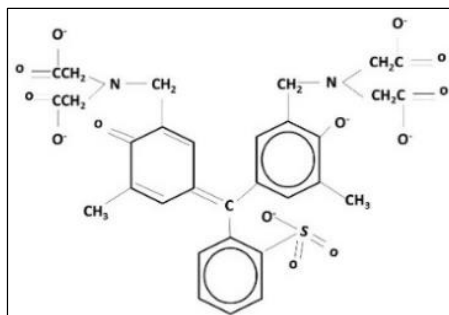


Fig 4a: Xylenol orange

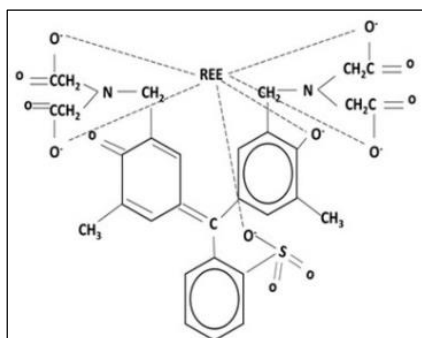


Fig 4b: REE xylenol orange complex

Complex formation depends on the solution acidity. REEs are coordinated to the xylenol orange through the iminodiacetic moiety and phenolic group [22]. At lower pHs protonation of these groups prevents the chelation between xylenol orange and REEs. As the pH is increased from 2, the protonation tendency decreases and complex formation increases. From pH 3 onwards REEs are quantitatively converted into xylenol orange complex.

Optimum amount of adsorbent required for quantitative adsorption of all the REEs and Y were 50 mg as evident from fig 5.

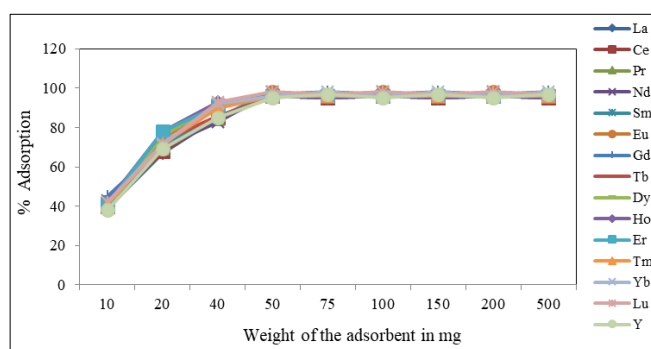


Fig 5: Variation of % adsorption of REEs onto SMXO with weight of adsorbent

Like in all solid phase extraction studies, amount of adsorbent required for adsorption is very less in this method also. This is due to the high sorption /retention capacity of SMXO for REEs. The sorption capacity ( $q_e$ ) of SMXO for individual REEs is the amount of the element required for the saturation of 1 gram of the synthetic sorbent in (mg/g). It was determined by the following equation:

$$q_e = (X-Y)/Z$$

Where X is the amount of rare earth element added, Y the amount remaining in the solution after adsorption and Z the weight of the adsorbent.

Table 4: Adsorption capacities for individual REEs

Element	Sorption capacity (mg/g)
La	2.0
Ce	2.0
Pr	2.2
Nd	2.3
Sm	2.3
Eu	2.3
Gd	2.4
Tb	2.4
Dy	2.5
Ho	2.5
Er	2.7
Tm	2.8
Yb	2.8
Lu	3.0
Y	2.5

The sorption capacity of the SMXO for different REEs ranges from 2-3mg g<sup>-1</sup> (table-4). Adsorption capacity gradually increases from La to Lu with increase in atomic number. Adsorption capacities observed for SMXO is higher compared to that obtained for the adsorbent prepared by coating silica gel with reagent in presence of CTAB

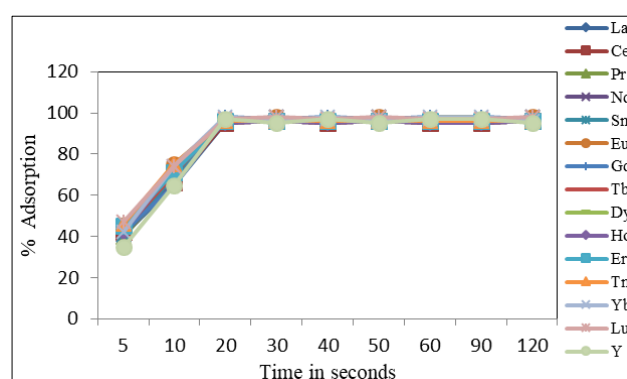


Fig 6: Variation of adsorption with time

Quantitative adsorption of REEs onto SMXO takes after a contact time of 30 minutes (fig 6).

The elution of REEs from SMXO was examined using different concentration of various acids and complexing agents. The results are given in fig 7.

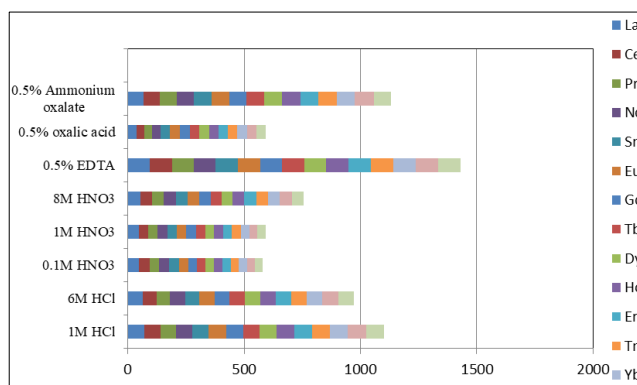


Fig 7: % Elution of REEs from adsorbent using different reagents

It is evident from the fig 7 that EDTA gave quantitative recoveries compared to other complexing agents. Thus 0.5% (w/v) EDTA was selected as the eluent for REE pre-concentration using SMXO. Further experiments showed that 5 mL of 0.5% EDTA was sufficient for the quantitative elution of REEs from SMXO. EDTA was able to quantitatively elute REEs adsorbed onto SMXO because EDTA forms stronger complexes with REEs compared to xylenol orange. Formation constants of REE- EDTA ( $\log K_f$ ) complexes ranges approximately from 16-20 while that of xylenol orange is 5-6 [23].

Experiments were carried out to find the effect of different major elements on the adsorption of REEs on to SMXO. Up to 1mg/mL of Na, K, Ca, Mg and Ti did not affect the adsorption of REEs to SMXO. Aluminum and iron when present above 200 mg/L, adsorption of REEs were reduced to 30%. This reduction can be attributed to the formation of strong Al and Fe(III)-xylenol orange complexes at pH 3 [24, 25]. These elements when present at higher concentration preferentially form their complexes with xylenol orange there by reducing the formation of REE-xylenol orange complex. It is reported that Fe (II) does not form complex with XO [26]. Hence reduction of Fe (III) in presence of REEs with different reducing agents and their adsorption to SMXO were studied. It was observed that the addition of hydroxylamine hydrochloride was able to eliminate the interference of iron. Aluminum interference was eliminated by fusing rock samples with NaOH and leaching the melt with water to remove Al as sodium aluminate.

Accuracy of the procedure was checked by comparing values obtained for certified reference materials SY-2 and SY-3. Results obtained (table-5) are in agreement with the certified values. Some selected rock samples were analysed for REE content by the proposed procedure and cation exchange chromatography. Results obtained (table-6) are in agreement with each other. Accuracy expressed as % error ranged between 1-5%. The precision of the method, expressed as the relative standard deviation (RSD) is 2-5% (table-7).

**Table 5:** Recovery studies of REEs and Y ( $\mu\text{g/g}$ ) by the proposed method, for the CCRM reference materials Sy-2 and Sy-3

Element	SY-2		SY-3		% Error
	By Proposed method	Reported	By Proposed method	Reported	
La	73 $\pm$ 3	75	1324 $\pm$ 35	1340	$\pm$ 1-3
Ce	170 $\pm$ 5	175	2300 $\pm$ 63	2230	$\pm$ 1-3
Pr	17.5 $\pm$ 1	18.8	210 $\pm$ 14	223	$\pm$ 3-5
Nd	71 $\pm$ 2	73	708 $\pm$ 14	670	$\pm$ 0-4
Sm	15.5 $\pm$ 0.8	16.1	110 $\pm$ 8	109	$\pm$ 1-4
Eu	2.3 $\pm$ 0.08	2.4	16.5 $\pm$ 0.3	17	$\pm$ 1-5
Gd	16.4 $\pm$ 0.7	17	110 $\pm$ 8	105	$\pm$ 3-5
Tb	3.0 $\pm$ 0.8	2.5	17 $\pm$ 1.6	18	$\pm$ 4-5
Dy	17.5 $\pm$ 0.6	18	115 $\pm$ 8	118	$\pm$ 2-4
Ho	4 $\pm$ 0.9	3.8	27 $\pm$ 3.5	29.5	$\pm$ 4-5
Er	13 $\pm$ 0.9	12.4	70 $\pm$ 5	68	$\pm$ 1-3
Tm	2.0 $\pm$ 0.3	2.1	11 $\pm$ 1.1	11.6	$\pm$ 3-5
Yb	17.3 $\pm$ 0.2	17.0	60 $\pm$ 3.2	62	$\pm$ 0-2
Lu	2.8 $\pm$ 0.1	2.7	7.2 $\pm$ 0.7	7.9	$\pm$ 1-3
Y	123 $\pm$ 3	128	710 $\pm$ 6	718	$\pm$ 2-3

**Table 6:** Comparison of REE values in  $\mu\text{g/g}$  obtained for some rock samples by proposed method and by ion exchange method

Element	Sample-1		Sample-2		Sample-3	
	By proposed method	By ion exchange separation	By proposed method	By ion exchange separation	By proposed method	By ion exchange separation
La	63 $\pm$ 3	67 $\pm$ 2	46 $\pm$ 2	50 $\pm$ 1	111 $\pm$ 4	116 $\pm$ 3
Ce	144 $\pm$ 4	156 $\pm$ 3	114 $\pm$ 4	121 $\pm$ 3	239 $\pm$ 6	247 $\pm$ 4
Pr	16 $\pm$ 1	18 $\pm$ 1	13 $\pm$ 1	14 $\pm$ 1	24 $\pm$ 1	25 $\pm$ 1
Nd	60 $\pm$ 2	65 $\pm$ 1	47 $\pm$ 2	52 $\pm$ 1	86 $\pm$ 2	94 $\pm$ 1
Sm	15 $\pm$ 0.8	17 $\pm$ 0.6	13 $\pm$ 0.8	14 $\pm$ 0.6	20 $\pm$ 0.8	21 $\pm$ 0.6
Eu	2.0 $\pm$ 0.08	2.3 $\pm$ 0.05	1.5 $\pm$ 0.08	1.7 $\pm$ 0.05	2.9 $\pm$ 0.08	3.2 $\pm$ 0.05
Gd	18 $\pm$ 0.7	13 $\pm$ 0.5	14 $\pm$ 0.7	11 $\pm$ 0.5	20 $\pm$ 0.7	14 $\pm$ 0.5
Tb	1.9 $\pm$ 0.5	2.7 $\pm$ 0.5	2.0 $\pm$ 0.5	2.3 $\pm$ 0.5	2.0 $\pm$ 0.5	2.7 $\pm$ 0.5
Dy	11 $\pm$ 0.6	13 $\pm$ 0.5	10 $\pm$ 0.6	11 $\pm$ 0.5	8.0 $\pm$ 0.6	8.3 $\pm$ 0.5
Ho	2.0 $\pm$ 0.6	3.0 $\pm$ 0.4	1.9 $\pm$ 0.6	2.6 $\pm$ 0.4	1.0 $\pm$ 0.6	1.8 $\pm$ 0.4
Er	11 $\pm$ 0.8	9.0 $\pm$ 0.6	10 $\pm$ 0.8	8.0 $\pm$ 0.6	7.0 $\pm$ 0.8	5.8 $\pm$ 0.6
Tm	1.2 $\pm$ 0.2	1.6 $\pm$ 0.2	0.5 $\pm$ 0.1	0.3 $\pm$ 0.1	0.4 $\pm$ 0.1	0.3 $\pm$ 0.1
Yb	8 $\pm$ 0.1	8.0 $\pm$ 0.1	6.0 $\pm$ 0.1	6.0 $\pm$ 0.1	2.8 $\pm$ 0.08	2.6 $\pm$ 0.08
Lu	1.6 $\pm$ 0.1	1.2 $\pm$ 0.1	1.6 $\pm$ 0.1	1.2 $\pm$ 0.1	1.4 $\pm$ 0.1	1.0 $\pm$ 0.1
Y	72 $\pm$ 3	78 $\pm$ 2	65 $\pm$ 3	68 $\pm$ 2	35 $\pm$ 3	37 $\pm$ 2

**Table 7:** Determination limit of REEs by proposed method and % RSD at this level

Element	Determination limit $\mu\text{g/mL}$	%RSD N=4	Element	Determination limit $\mu\text{g/mL}$	%RSD N=4
La	2.5	2.2	Dy	1.0	3.4
Ce	2.5	1.7	Ho	1.0	3.6
Pr	5.0	5.1	Er	1.0	2.8
Nd	2.0	2.0	Tm	0.75	3.6
Sm	1.2	3.0	Yb	0.25	4.6
Eu	0.2	3.7	Lu	0.25	4.9
Gd	1.5	3.7	Y	0.5	4.7
Tb	1.5	2.0			

## Conclusion

A novel single -step synthesis procedure for silica modified with xylenol orange has been developed. The synthesized adsorbent has been applied for the pre-concentration, separation and determination of REEs in rock samples. NaOH fusion of the rock samples followed by water leaching and adsorption of REEs to SMXO in presence of ascorbic acid at pH 3 and elution with 0.5% (w/v) EDTA facilitated the pre-concentration of REEs and its separation from major elements in rock samples. The adsorbent has a very high extraction rate for REEs with its loading half time was less than 15 sec. This adsorbent has a good potential to separate REEs from high concentration of alkali, alkaline earth and other anions present in rock samples. This method is very simple and the sorption capacity of the adsorbent for different REEs is much higher (40-50%) than other common adsorbents. The obtained result after the application of the method to certified reference materials indicates a very good accuracy (% Error  $\pm$  1-5) and reproducibility (% RSD 2-5%).

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