http://www.e-journals.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 4, No. 3, pp. 381-384, July 2007

Online Determination of Sm, Eu and Yb in Environmental Samples by Inductively Coupled Plasma – Optical Emission Spectrometry

J. DILIP KUMAR, P. REDDY PRASAD, B. KRISHNA PRIYA,
P. SUBRAHMANYAM S. RAMANAIAH[#] and P. CHIRANJEEVI[*]

[*]Environmental Monitoring Laboratory,
Department of Chemistry,

[#]Department of Geology
S. V. University, Tirupati-517 502, A.P., India.

Received 14 December 2006; Accepted 10 January 2007

Abstract: A procedure was developed for the determination of Sm, Eu and Yb in water samples by inductively coupled plasma-optical emission spectrometry (ICP-OES) after preconcentration on synthesized 5-(4-pyridyl azo)-8-quinolinol supported by Borassus flabellifer inflorescence (BFI). The sorbed element was subsequently eluted with 0.4 M HNO_3 and the acid eluates were analyzed by ICP-OES. Under the optimal conditions, Sm, Eu and Yb in aqueous samples were concentrated 100-fold. Recoveries were obtained by the proposed method in the range of 98.6 -99.8%. This method was also applied for the analysis of spiked and natural water samples. The results provide strong evidence to support the hypothesis of an adsorption mechanism.

Keywords: Samarium (Sm), Europium (Eu), Ytterbium (Yb), 5-(4-pyridyl azo)-8-quinolinol, Borassus flabellifer inflorescence (BFI), Natural water samples, Inductively coupled plasma-optical emission spectroscopy

Introduction

The inductively coupled plasma-optical emission spectrometry (ICP-OES) technique, which offers fast multi-elemental analysis, suffers from a poor sensitivity. The preconcentration method provides lower detection limits and also helps to avoid the matrix interferences in the determination of elements present in water samples. This drawback can be rectified by a

combination of a suitable on-line preconcentration technique with subsequent ICP-OES determination. Various preconcentration methods for the determination trace metals by AAS, based on solvent extraction[1], various chromatographic techniques[2] and sorbent extraction[3, 4], have been developed and discussed in the literature. Hence the present investigation a new online column separation and preconcentration method for determination of lanthanide metals.

Experimental

Instrumentation

Atomic emission spectrometer ICP-OES Varian, Liberty series 11, was used. The plasma was run at 700V with 15 l/min Ar. The operating conditions and wavelength of the emission lines examined are listed in Table 3. An Elico model Li – 129 pH meter with combined glass and calomel electrode was used for pH measurements.

Synthesis of reagent

The reagent 5-(4-pyridyl azo)-8-quinolinol was obtained by complexation of 4- Amino pyridine with 8-quinolinol in acidic medium at 0-5 ^{o}C as described previously for similar reagents [6,7]. For diazotization 0.91g of 4-amino pyridine was dissolved in 50 mL of aqueous ethanol and 2% sodium nitrite of 10mL was added dropwise and stirred at 0-5 ^{o}C for 1h. For coupling, 1.45 g of 8-quinolinol was dissolved in 50mL of aqueous ethanol and the mixture was cooled to 0-5 ^{o}C. The system was allowed to stand overnight in refrigerator at 0-5°C. The resulting yellow precipitate was filtered and purified by recrystalization with ethanol. The yield was 88% and melting point of the product is 165-170 ^{o}C.

Column preparation

Medical syringe (20 mL) was used as column. The support was prepared from Borassus flabellifer inflorescence in the following manner; 1-cm thick segments with diameter of 2.5cm were cut. The segments were soaked in 0.4M HNO_3 for 12 h, washed in deionized double distilled water and dried prior to use. The syringes were then filled with the air-dried sigments. The column consisted of 7-8 separate segments then 2g of solid 5-(4-pyridyl azo)-8-quinolinol was introduced between segments. This amount of complex forming agent was necessary to retain the 100 µg of each element in 200 mL of sample.

Procedure

The method was tested with model solutions before its applications to real samples. 200 mL of a standard Sm, Eu and Yb metal solutions (0.04 µg mL $^{-1}$) buffered at pH 7.0±0.2 with phosphate buffer, was passed through the column by opening the position 1 of valves A and B at a flow rate of 7 mL /min. after passing the solution the position 1 of the valves Aand B were closed automatically, and position 2 of valve A and B were opened. Adding 5mL of 0.4M HNO_3 through the column with a flow rate of 1 mL /min performed elution. The acidic eluents were collected in a metal-free polythene bottle and neubilized into the plasma of ICP-OES.

Results and Discussion

5-(4-Pyridyl azo)-8-quinolinol specific complexing ligand for analytical determination of Sm, Eu and Yb at pH 7.0±0.2. The extractability of metal complex of 5-(4-pyridyl azo)-8-quinolinol in 5 mL of 0.4M of HNO_3 medium is more convenient. This proposed method was employed for different natural water samples. The samples were filtered through cellulose membrane of pore size 0.45µm. For each sample, 200 mL of natural water samples was passed through the column as explained procedure in the experimental part and results of natural water

samples are shown in Table.1. Then spiked water samples were prepared with 2 L of distilled water, by adding known amounts of standard solutions, preconcentrated and determined by earlier discussed procedure. Percentage recoveries of Sm, Eu and Yb are shown in Table 2.

Table 1. Metal ions of analytical result in natural water samples.

Elements found µg/mL	Present method				Standard method[5]
	Name of the sampling areas				
	Industrial steel plant area		krishnapatnam area		
	Sample-I	Sample-II	Sample-I	Sample-II	
Sm	71	68	40	39	70
Eu	50	53	32	37	51
Yb	47	49	29	31	45

Table 2. Recovery of heavy metals from different concentration of spiked water samples

Element	Concentration of each element added, 10ng/L			Concentration of each element added, 30ng/L			Concentration of each element added, 50ng/L		
	Found ng/L	Recovery %	RSD %	Found ng/L	Recovery %	RSD %	Found ng/L	Recovery %	RSD %
Sm	9.98	99.8±.0.3	2.60	29.6	98.6±0.2	2.44	49.5	99.0±0.5	2.53
Eu	9.95	99.5±0.2	2.48	29.8	99.3±0.3	2.56	49.4	98.8±0.1	2.44
Yb	9.96	99.6±0.4	2.52	29.7	99.0±0.1	2.47	49.8	99.6±0.2	2.54

Table 3. Operating parameters of ICP-OES

Photomultiplier tube voltage, V	700
Incident power, kW	1.1
Plasma gas flow, L/min	1.5
Auxillary gas flow, L/min	1.5
Observation height , mm	14.0
Pump rate, mL/min	15.0
Sample uptake time, s	25.0
Wavelength of elements	
Sm	325.7
Eu	380.6
Yb	410.5

Influence of pH

Effect of pH on the preconcentration of metal ions was studied by on-line determination of 20 µg of individual elements in the pH range of 2.0-9.0 and by introducing 2.0g of 5-(4-pyridyl azo)-8-quinolinol between BFI segments. The data of the pH effect for various elements are shown in Figure 1. At pH 7.0±0.2, the maximum recovery was obtained.

Efficiency of elution

The simultaneous determina tion of the preconcentrated element by ICP-OES, the elution was performed with 0.05-0.5M HNO_3. Quantitative multi element elution was achieved with 0.4M HNO_3. Hence, 5 mL of 0.4M HNO_3 was chosen as the optimum eluent for the multi-elemental determination, and recoveries were 100%.

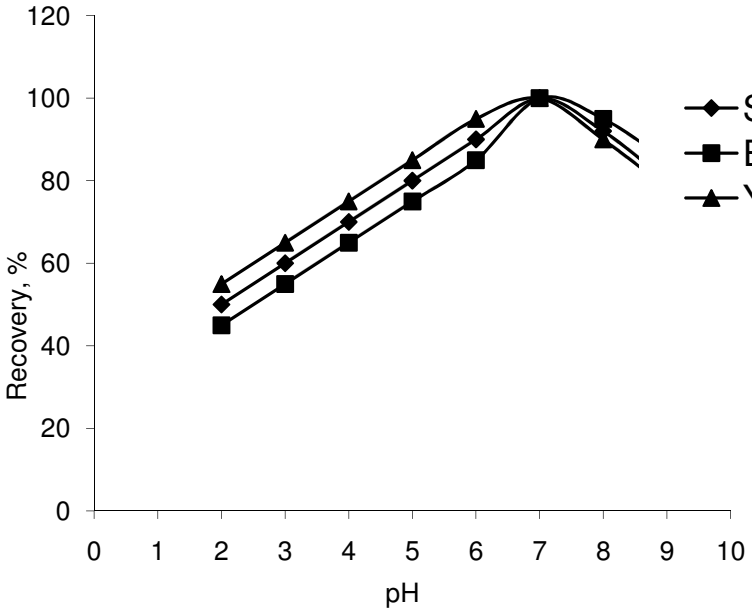

Figure 1. Effect of pH on the complexation of metal ions with reagent

Effect of volume of sample on elution

The effect of the sample volume on the extraction of Sm, Eu and Yb was studied by taking different volumes of water samples of 50-500 mL. In this case, the recovery was 99.90% at 200 mL volume. Hence, 200 mL of water sample was chosen for the present study.

Conclusions

The method developed is simple, selective, sensitive and reproducible for preconcentration and determinations of Sm, Eu and Yb. The modified BFI material is stable, convenient and reproducible for four times made the method as cost less. The relative standard deviation for four independent determinations reached values of 2.44-2.60 for individual solutions of different concentrations. The recoveries from spiked water samples were in the range of 99.00-99.90%.

References

1. Backstrom K, Danielson L G and Nord L, *Analyst*. 1984, **109,** 323.
2. MacCarthy P, Klusman R W, Cowling S W and Rice J A, *Anal.Chem.*1991, **63, 301.**
3. Welz B, *Microchem. J.* 1992, **45,** 163.
4. Ali A, Ye Y, Xu G, Yin X and Zhang T, *Microchem. J.* 1999, **63,** 365.
5. Standards methods for examination of water and waste water, 9th Ed, APHA, AWWA & WEF, Washington D C, U S A, 1995, 3-16.
6. Hovind H R, *Analyst.* 1975, **100,** 769.
7. Lemos V A, Baliza P X, Yamaki R T, Rocha M E, and Alves A P O, *Talanta.* 2003, **61**(5), 675.