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Determination of Some Lanthanides Ion Coeluent with the Transient Metals by Ion Chromatography.

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ABSTRACT

The lanthanide metals are detected by measuring the absorbance at 530 nm of a complex formed with the post column PBHA reagent .Using this method , transient metals will co-eluent with the lanthanides. Rapid, efficient, cost effective and reproducible isocratic reversed phase method has been developed and validated for the determination of lanthanides in active inorganic ions using mobile phase of 1:3 v/v diglycolic acid and oxalic acid as a mixture having a pH of (4.5). The Mobile phase was pumped at a flow rate of 1.5 mL min^{-1}using isocratic elution through Ion Pac ,Cs$_{18}$ (250×2 mm, 5 μm) column. UV detection was performed at 530 nm. The method was validated following the IC Isocratic .A linear calibration curve was obtained over the concentration range(0.1 – 1) ng mL^{-1}(n=3) with correlation coefficient of 0.9999. The detection limits and the quantitation are as follow: 10.523, 10.525, 10.528, 10.677, 10.526, 10.525, 10.522 and 10.528 ng mL^{-1}and 31.890, 31.894, 31.903, 32.354, 31.898, 31.885 and 31.903 ng mL^{-1}for the standard material respectively. Recovery was found to be in the range 99-100% with the precision of less than 1%. The Developed method was successfully applied for the analysis of standard solutions and study the interactions of lanthanides with transition metals at 35°C

Keywords : IC Isocratic , interaction ,transition metals, UV detector and lanthanides

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INTRODUCTION

In general, Lanthanides has moderate trend to form complexes which is increased linearly with atomic number of the metals. Ions of these elements in its aqua solutions bonded with number of anions and by this way it formed stable complexes such as oxalate ($MC_2O_4^{-2}$) which is difficult to be separated from its aqua solutions owing to its high stability. In spite of the similarity in chemical behaviors of Lanthanide ions but , according to empiric proves , chelate reagents can be used due to high selectivity of lanthanide ions [1] . Stability was depend on pH values , when a mixture of Lanthanides ions are separated upon the relative stability constants. Separation of these ions by chromatography does not affected by slightly changes in temperature and pressure using weaken cations separation columns [2] . Lanthanide ions in aqua solutions are in the form as trivalent cations, having similar characteristics so it is not easy to be separated by ionic exchange method [3] , Therefore a chelate reagent such as oxalate were used to increase the selectivity of these ions by formation of stable oxalate- Lanthanide complex which form a weaken bounds with cation exchanger [4,5].

Two types of equilibrium are counted during cation exchange .One between the mixture and ionic exchanger and the other between lanthanides with lanthanides-reagents complexes [6], the later will allow these separation of lanthanides that has a relatively high stability constant with oxalate reagents such as La^{+3}, Ce^{+3} . Other lanthanides ions are strongly bounded in the mixture i.e. it needs longer time to elute such as Nd^{+3} and Yb^{+3}. On other hand ions which formed a weak complexes with oxalate will eluted firstly. Generally lanthanides ions have longest time in the exchanger and mixture [7] . Using strong complexing reagent lead to the formation of lanthanides anions and under such conditions , Lanthanides ions can be separated by anion exchangers, These stronger complexes are more electro negativity and also from electronic displacement which will be inverse to forming separated positive ions[8]. In this technique a new separation of lanthanides ions such as cation and anion exchange were found to be depended upon the ratio of lanthanide elements [9] . Anionic exchange is the most preferable method for transitional lanthanide elements by photometric method at wavelength 525 nm with ($\varepsilon= 5.1\times10^3$ L.mole^{1}cm^{-1}) by applying Post-Column reaction to form metal complex (PBHA) N-Phenyl benzohydroximic acid [10] so that the detection limit for this method was ranged from ($1x10^{-5}$ – $1x10^{-3}$) ppm using 100 μl sample volume [11] .

Standard Solutions

500 mg/liter of lanthanides ions were prepared by dissolving an accurate weight of lanthanide chloride and diluted to one liter using double distilled water and the pH of the solution was adjusted to 4 — 4.5.

Anion Exchange separation of Lanthanides metals

Analysts

La^{+3}, Ce^{+3}, Nd^{+3}, Yb^{+3}.

Method

Separation column used in this method is an Ion Pac CS_{18} and the linear gradient oxalic acid concentration ranged between (16.5-22.5)mM with total time of separation is 30 minutes.

Lanthanide elements can be detected at a wave length 525 nm for anions complexes with oxalic acid and diglycolic acid with reagent PBHA . This reagent must be kept under effect of He or N_2 gas [12] .

Recommended Equipment's

Ahome - made designed IC by metrohm 690 with two detectors (conductivity and UV . Vis) and LKB Isocratic pump C2150.
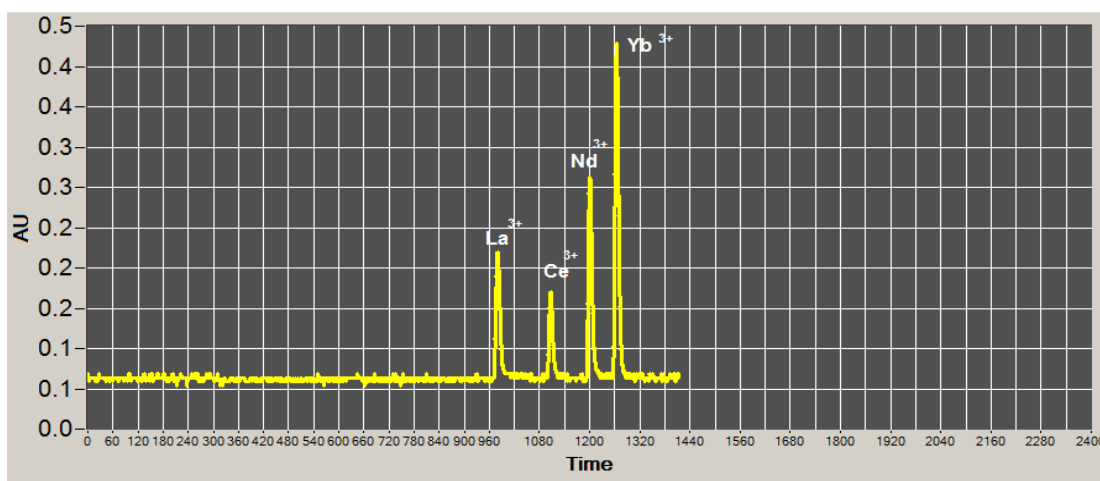
Simultaneous Separation of transition metals and Lanthanide metals

Analysts

A mixture of Fe^{2+} , Cu^{2+}, Ni^{2+}, Zn^{2+}, La^{+3} ,Ce^{3+},Nd^{+3}, Yb^{+3}. Were used. The experiment parameters and conditions were listed in table **1**

Table 1: Method's parameter

Parameters	Conditions
Description Column	Ion Pac CS$_{18}$, 2 mm CSRS® ULTRA II 2 mm, Auto Suppression® recycle mode *(P/N* 060478*)*
Iso Critic Mobil phase	Oxalic acid with reagent PBHA
Detection System	UV detection
Wave length Maximum	525 nm
Flow Rate	1.5 mL / min
Temperature	30 °C
pressure Background	151 Bar
Run Time	30 Min
Injection Volume	100µL

Figure 1: Separation of lanthanides by anion exchange
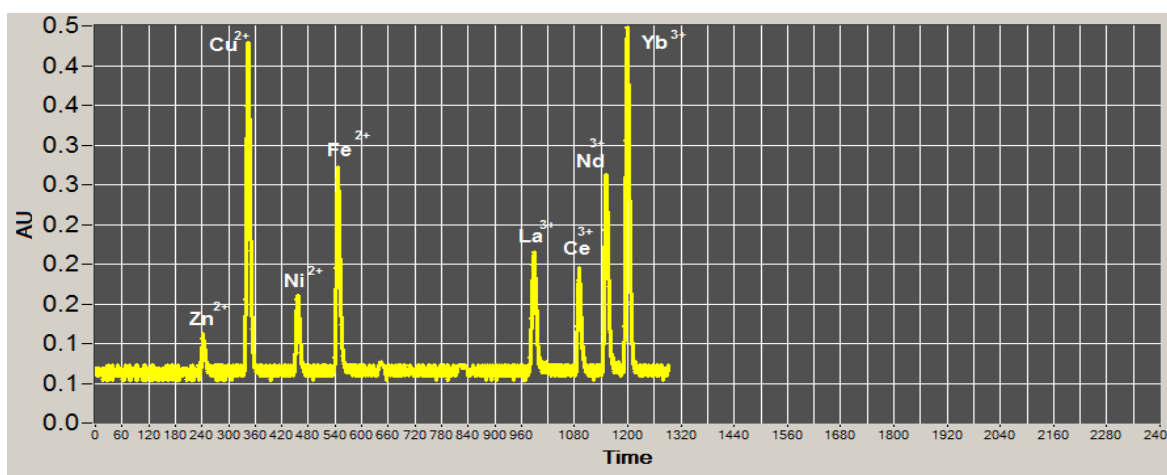
Figure 2: Separation of lanthanides and transition metals in a single injection by ion chromatography.

DISCUSSION

Lanthanide ions can be separated by applying anion-cation simultaneous exchange technique[13] and an aqua solutions of a number of d-orbital groups were used in this research which can be achieved by Chromatography separation benefiting on the electronic selectivity differences between two types of group (d and f) elements[14]. The mono and divalent anions of transition elements form a selective stable complexes with sulphosalycilic acid and with 18-Crown-6 Ether which allowed separation, while lanthanide elements were remained non-separated in the column and upon a time of displacing transition elements ions , it was displaced with the most stable complex using oxalate mixture and diglycolic acid . Total time for both ions elements (d and f) was found 30 minutes and that lanthanide elements can be detected by measuring absorption at 525 nm upon forming PBHA complex.

A linear calibration curve was obtained by plotting the absorbance for six standard solutions in the range (1 to 10) x 10^{-4} ppm against peak height for each ion and the intercept and the slope were calculated.

Detection limits and Quantitation

Detection limit (D.L.) and quantitation (OQ) are the concentrations that give signal to noise ratio of 2:1 and 10:1 respectively, which can be detected and verified by the relation of standard deviation of response (SD) to the slope of calibration (S) [15].

The detection limit is 3.3.SD/S and quantitation is 10 SD/ S

Table (**2**) shows the regression statistics of the proposed method

Table 2: Regression statistics of the proposed method with D.L, OQ, Intercept and Slope for lanthanide metal.

Ions	Retention Time(min)	R^2	Std Er[a] $(10^6) \times$	StdErEst[b] $(10^6) \times$	Intercept $(10^6) \times$	Slope $(10^6) \times$	D .L ng mL^{-1}	OQ ng mL^{-1}
La^{+3}	16.6	1.00	3.577	4.1925	1.033	6.872	10.523	31.890
Ce^{+3}	18.2	0.999	0.473	0.5537	-0.475	6.554	10.525	31.894
Nd^{+3}	19	0.999	1.184	1.3294	0.967	10.928	10.528	31.903
Yb^{+3}	20.2	0.971	31.836	37.3160	77.836	60.761	10.677	32.354

[a]standard error, [b]standard error estimate

Table 3: Regression statistics of the proposed method with D.L, OQ, Intercept and Slope for transient metals will co-eluent with the lanthanides

Ions	Retention Time(min)	R^2	Std Er[a] $(10^6) \times$	Std Er Est[b] $(10^6) \times$	Intercept $(10^6) \times$	Slope $(10^6) \times$	LOD ng mL^{-1}	LOQ ng mL^{-1}
La^{+3}	16.5	1.000	3.577	4.1925	1.033	6.872	10.523	31.890
Ce^{+3}	18.2	0.999	0.473	0.5537	-0.475	6.554	10.525	31.894
Nd^{+3}	19	0.999	1.184	1.3294	0.967	10.928	10.528	31.903
Yb^{+3}	20.2	0.971	31.836	37.3160	77.836	60.761	10.677	32.354
Zn^{+2}	4	0.999	0.303	0.3553	-0.915	3.708	10.526	31.898
Cu^{+2}	5.7	0.999	1.532	1.7962	1.019	19.908	10.525	31.895
Ni^{+2}	7.7	1.000	0.0	0.0	6.36E-15	5.000	10.522	31.885
Fe^{+2}	9	0.999	1.197	1.4026	3.033	11.672	10.528	31.903

All peaks where well resolved and the precision was acceptable. System suitability of the method was studied through method development by calculating D.L, OQ, Intercept , Slope, Retention time standard error, The standard error estimate and repeatability favorable for the system are summarized in Tables **1, 2** and **3**. The values in table **3** was referred to high accuracy and successful of the proposed method.

Linearity and range

Linearity of the method was tested in order to demonstrate a proportional relationship of response verses analyzed concentration. A six concentrations in the range (0.1-1.0) x 10^{-4} ppm with^{-1} (n=3) were used. The regression equation was found linear by plotting peak area verses lanthanides concentration, correlation coefficient obtained for the lanthanides and transient metals obtained for the regression line was greater than 0.999. Table **2** represents the regression data including, correlation coefficient, slope, intercept, standard error and standard error estimate .

Accuracy and recovery

The accuracy of an analytical method is determined by how close the test results obtained by that method to the true value. It can be determined by recovery studies, where a known amount of standard is spiked in the sample to be analyzed [16]. The results are shown in Table **3** and it is evident that the method is accurate within the desired range .

Table 4: Accuracy and recovery for the studied elements

Ions	Recovered conc. ($\mu g\ mL^{-1}$)	% Recovery	%RSD
La^{+3}	3.00	99	0.84
Ce^{+3}	2.99	99	0.77
Nd^{+3}	2.98	98	0.75
Yb^{+3}	2.98	100	1.12
Zn^{+2}	3.00	99	0.81
Cu^{+2}	2.98	98	0.75
Ni^{+2}	3.00	100	0.76
Fe^{+2}	3.00	100	072

Precision [17,18]

Precision of method, reported as %RSD, was estimated by measuring repeatability (intra-day assay) on seven replicate injection at concentration of $3\times10^{-4}\mu g\ mL^{-1}$ in Table **4**, and intermediate precision (inter-day variation) was studied for two days using concentration solution of $3\times10^{-4}\mu g\ mL^{-}$ (n=7). All the results were given in table **5.**

Table 5: Intra and inter-day precision and accuracy of analyzes added $3\times10^{-4}\ \mu g\ mL^{-1}$ (n=7) .

Ions	Intra-day			Inter-day		
	Found $\times10^{-4}$	%RSD	%Rec	Found $\times10^{-4}$	%RSD	%Rec
La^{+3}	3.00	0.84	99	2.99	0.79	99
Ce^{+3}	2.99	0.77	99	2.98	0.77	98
Nd^{+3}	2.98	0.75	98	2.89	0.77	98
Yb^{+3}	2.98	1.12	100	2.88	1.10	99
Zn^{+2}	3.00	0.81	99	2.98	0.81	98
Cu^{+2}	2.98	0.75	98	2.97	0.80	98
Ni^{+2}	3.00	0.76	100	9.98	0.79	99
Fe^{+2}	3.00	072	100	2.99	074	99

CONCLUSION

A simple, rapid, accurate, precise, low cost and least time consuming HPLC method for the quantitative analysis of the lanthanide metals in standard solutions, has been developed and validated. The intra-run and inter-run variability and accuracy results were found in acceptable limits. Simplicity of the method[19] , shorter run time, economical nature and low limits of detection and quantitation makes the method superior to the other reported HPLC methods. The method could be applied analysis of studied

inorganic materials. The method has been applied to study cations metal interactions and the results reveal that the presence of metals ion has a more pronounced effect on availability of cations and complexation is the main factor responsible for decreased or increased availability of cation [20] . Therefore, a concomitant administration of transition metals with lanthanides seem advisable, Moreover, a proper time interval should be maintained.

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