

# Analytical method for detecting and estimating of lanthanide ions paired with transitional elements

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## HIGHLIGHTS

- An improved and sensitive method of lanthanides chromatography.
- Chemically stable complex with constant retention time separated by chromatography.
- A mathematical method was used in estimating linearity, accuracy, and recovery to confirm the success of lanthanides chromatography.
- Optimum conditions of chromatographic separation in lanthanides coelut with transient metals chromatography.

## Abstract

**Context:** A simple, specific, precise, and stability-indicating high-performance liquid chromatographic method for chemical analysis of lanthanide ions is detected by measuring the absorbance at 350 nm. The first complex ion lanthanide ions with oxalic acid to obtain very covalent and stability ions in complex, the second-step stability ions in complex formed with 18-crown-6-ether. Using a validated stability analysis method to separation and estimation, transient metals will coelut with lanthanide ions. **Objective:** A rapid, efficient, cost-effective, and reproducible isocratic reversed-phase method has been developed and validated for the determination of lanthanides in active inorganic ions. **Materials and Methods:** Using mobile phase methane sulfonic acid at pH 3.0, mobile phase was pumped at a flow rate of 1.0 mL min<sup>-1</sup> using isocratic elution through IonPac, CS18 (250 mm × 2 mm, 5 μm) column. Ultraviolet detection was performed at 350 nm. The method was validated following the IC isocratic. The standard calibration curve was linear in concentration range for all cations, lanthanides, and transient metals. **Results:** The correlation coefficient (R<sup>2</sup>) for the lanthanides and the transient elements at range (0.9971–1). Also, was studied the lower limits of detection and the lower limits of quantitation for the lanthanides and the Transient elements in the standard materials. Recovery was found to be in the range of 93–100% for all ions and the precision of <1%. **Conclusion:** The developed method was successfully applied for analytic analysis of standard solution and also to study the interaction of lanthanides and transient ions at the temperature (25°C).

**Key words:** Lanthanide ions, Stability separation method, Transition metals

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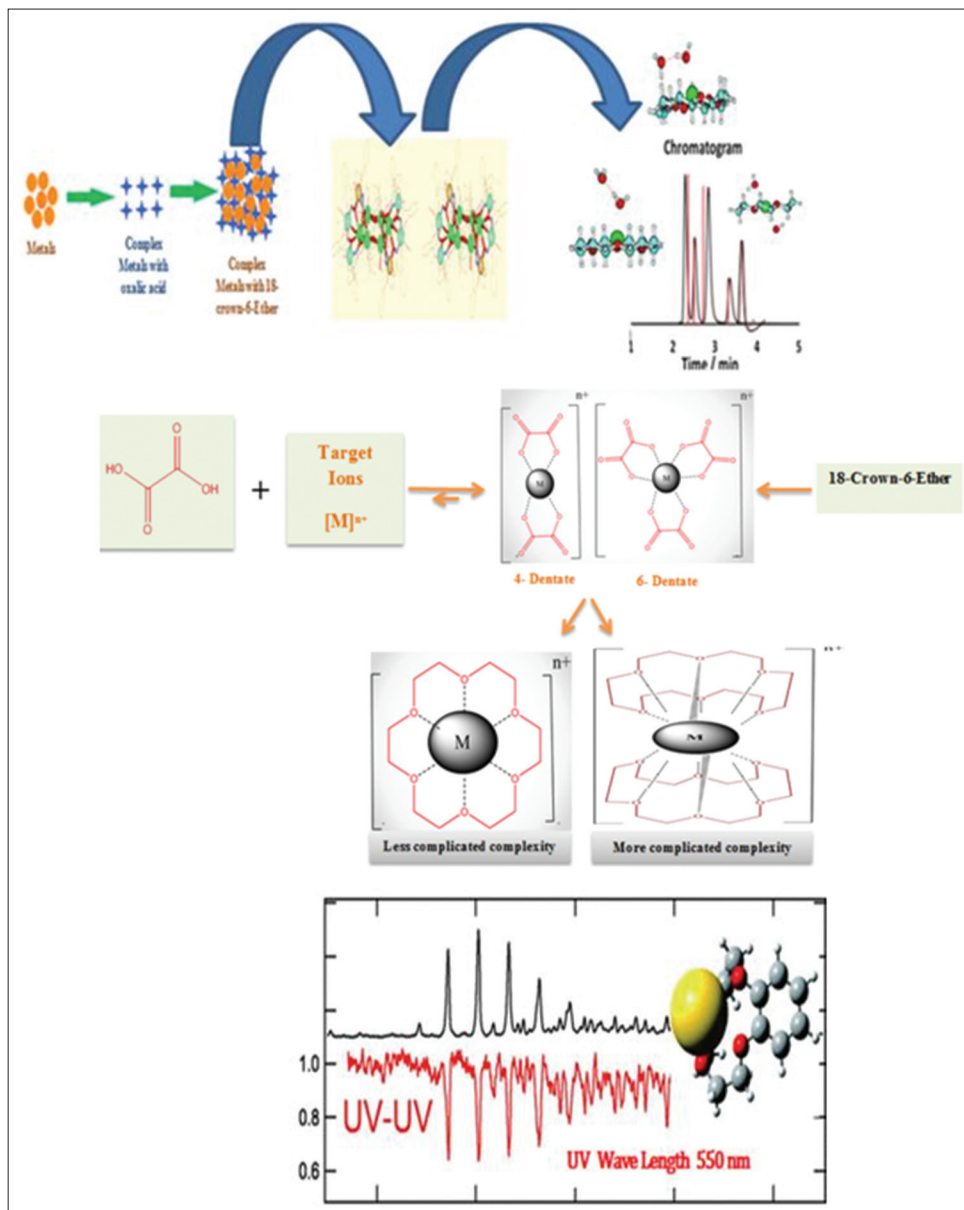
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## Graphical Abstract



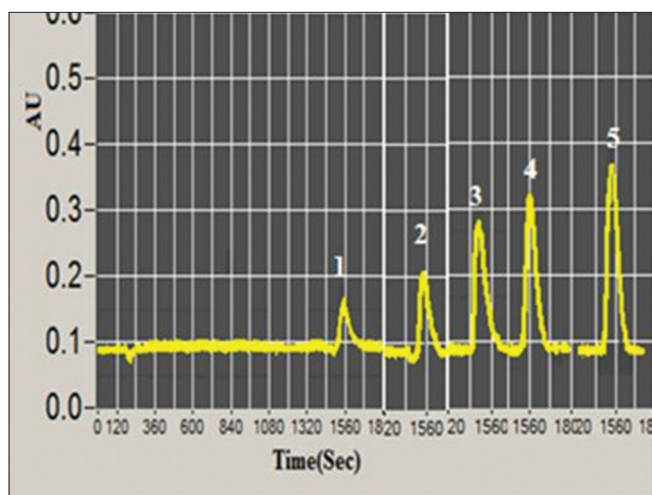
## INTRODUCTION

In general, lanthanides have a moderate trend to form complexes which are increased in linear with the atomic number of the metal. Ions of these elements in its solutions bonded with number of anions and by this way, complexes are stable such as oxalate ( $MC_2O_4^{2-}$ ) which is difficult to be separated from its solutions due to its high stability in spite of the similarity with chemical behave of lanthanides ions, but according to empiric proves, it can be used chalet reagents due to highly selectivity ions of these elements.<sup>[1,2]</sup> Stability is based on values of pH 3 when numbers of ions of these elements are separated and on constants of relative stability chromatography separation of these ions are not affected by slight changes in temperature and pressure by silica gel column, IonPac CS18 that contains microbeads resin.<sup>[3,4]</sup>

Solution of lanthanide ions is present in the form of double- and triple-parity cation as to that these characteristics are matched and it cannot be separated easily by ionic exchange,<sup>[5]</sup> as parity cations and thus, this selectivity of these ions is increased using chalet reagents such as oxalic acid<sup>[6]</sup> and that lanthanides are complexes with oxalic acid forming weaken bounds with cations exchangers.<sup>[7]</sup>

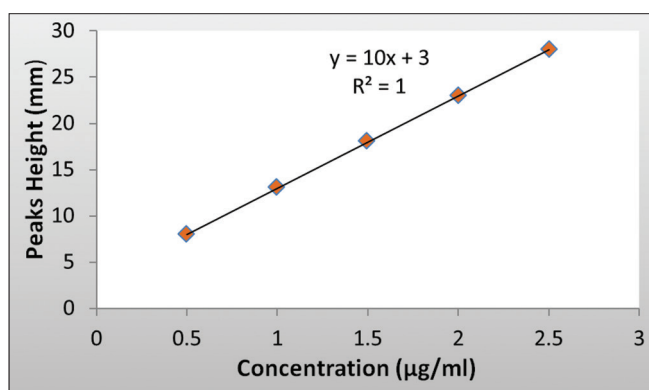
There are two states of balancing occurred during cation exchange which is the balance between the mixture and ionic exchanger and balance between lanthanides with lanthanide reagent's complexes.<sup>[8]</sup>

The second balance will allow separating lanthanides as to that lanthanide has relative stability constant with oxalic acid reagents, for example,  $La^{3+}$  and  $Eu^{2+}$  some lanthanides



Number of ions	Concentration ( $\mu\text{g/ml}$ )	Peaks height (mm)
1	0.5	8
2	1	13
3	1.5	18
4	2	23
5	2.5	28

**Figure 1:** Peaks height for standard calibration curve of  $\text{La}^{2+}$  ion



**Figure 2:** Standard calibration curve for  $\text{La}^{2+}$  ion

still longest period in the mixture ( $\text{Er}^{2+}$  and  $\text{Lu}^{3+}$ ) while ions formed weaken complexes with oxalate remaining lesser period rather than  $\text{La}^{3+}$  and  $\text{Eu}^{2+}$  in the mixture, lanthanide ions, in general, stay longest period in the exchanger and mixture.<sup>[9-11]</sup>

Using strong complex reagent leads to form lanthanides complexion under these conditions, lanthanides can be separated by silica exchangers as to that stronger complexes.<sup>[12]</sup> The new separation of lanthanides ions is depended on the ratio of lanthanide elements.<sup>[13]</sup>

The photometric method at wavelength 350 nm ( $\epsilon=5.34 \times 10^3$ ) by applying post-column reaction to form the metal complex with 18-crown-6-ether.<sup>[14,15]</sup>

## The Aim of Study

The aim of this study is to find a new method to have highly efficient, sensitive, easy, and quick to separation and qualitative a mixture of lanthanides ions and transient metals in different samples.

## Standards and Working Solutions

About 100  $\mu\text{g/ml}$  of lanthanides elements and 100  $\mu\text{g/ml}$  for transient metals which can be prepared in the laboratory or it is available commercially from chemical companies provided such these standard solutions used applying for chromatography absorption. Stock standard solution and five working solutions can be prepared for each ion, such these standard solution dissolved in the oxalic acid solution at pH values = 3 which can be applying chromatography.

Chloride metal for all cations, lanthanides, and transient metals in this experiment (d and f orbital).

18-Crown-6-ether was prepared as reagent in the concentration of 0.16 mM.

Deionized water is used by 18.2  $\text{M}\Omega$  cm to prepare standard solutions.

## Recommended Equipment

IC-ultraviolet by Metrohm 690 and LKB Isocratic pump C2150 were used.

## Separation of Lanthanide Metals

### Analytes

$\text{La}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Er}^{2+}$ ,  $\text{Lu}^{2+}$ .

## DISCUSSION OF THE METHOD

Separation column used in this method is IonPac CS18 and the linear gradient ranged between 36 and 38 min for the complex with 18-crown-6-ether as reagent while the total time separation for transient metals and lanthanides is 42 min shown in Figures 3 and 6.

Lanthanide elements can be detected under wavelength at 350 nm for complex ions with oxalic acid and 18-crown-6-ether as the reagent. This reagent can remain under the effect of  $\text{H}_2$  or  $\text{N}_2$  gas.<sup>[16,17]</sup>

## Simultaneous Separation of Transition Metals and Lanthanide Metals

### Analyts

$\text{Pt}^{2+}$ ,  $\text{Ir}^{2+}$ ,  $\text{Y}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Eu}^{2+}$ ,  $\text{Er}^{2+}$ ,  $\text{Lu}^{2+}$ .

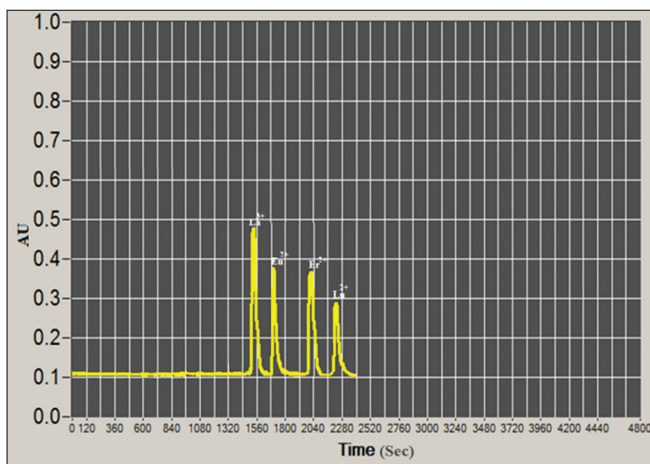
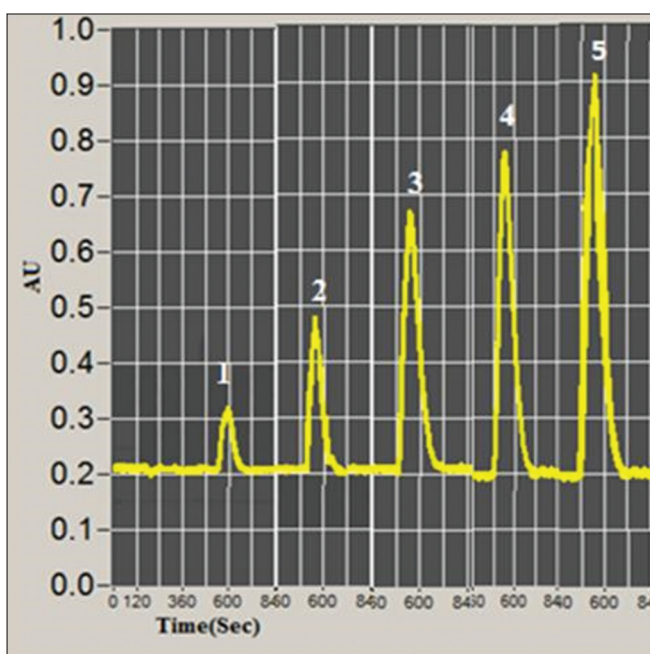


Figure 3: Graph peaks of separation lanthanides



Number of ions	Concentration (µg/ml)	Peaks height (mm)
1	0.3	10
2	0.6	22
3	0.9	33
4	1.2	42
5	1.5	52

Figure 4: Peaks height for standard calibration graph of Pt<sup>2+</sup> ion

Under the same conditions that were used to separate the elements of lanthanides shown in Table 1. A combination of transitional elements and lanthanides was separated. However, the total retention time of these elements, in this case, was increased, but the sequence of the appearance of lanthanides was not affected by the presence of transitional elements.<sup>[18,19]</sup> The success of the separation and estimation process for these elements with an 18-crown-6-ether shown in Figure 6.

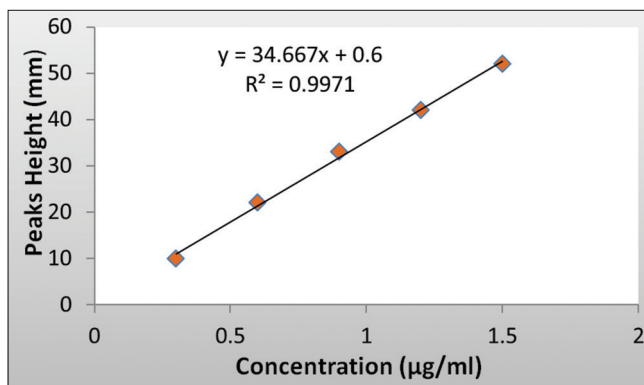


Figure 5: Standard calibration curve for Pt<sup>2+</sup> ion

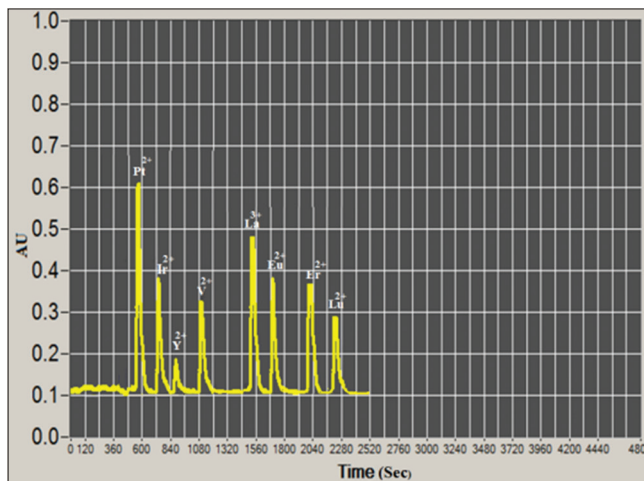


Figure 6: Graph separation of peaks lanthanide ions and transition metals

Table 1: Method's parameter

Parameters	Conditions
Description column	IonPac CS18, 2 mm CSRS ULTRA II 2 mm, Autosuppression recycle mode (P/N 060478)
Isocratic mobile phase	Oxalic acid complex with reagent 18-crown-6-ether
Detection system	UV detection
Eluent	0.16 mM methane sulfonic acid
Wavelength maximum	350 nm
Flow rate	1.0 ml/min
Temperature	25°C
Pressure background	180 bar
Run time	42 min
Injection volume	100 µL

An improved scheme of chelation ion chromatography system and a mixed eluent for the simultaneous determination of transition metals are described. A method based on the improved IC system and the mixed eluent (CH<sub>3</sub>SO<sub>3</sub>H)

for the analysis of eight ions in a single isocratic elution is developed. The optimize conditions which are different from references for analyte concentration and chromatographic separation are studied in detail.<sup>[20-22]</sup>

The same manner of La<sup>3+</sup> ion was used to obtain the calibration graph of La<sup>3+</sup>, Eu<sup>2+</sup>, Er<sup>2+</sup>, and Lu<sup>2+</sup> ions. The calibration graph was in the range of (0.5–2.5), (0.2–1.0), (0.2–1.0), and (0.1–0.5) µg/ml (*n* = 3) for La<sup>3+</sup>, Eu<sup>2+</sup>, Er<sup>2+</sup>, and Lu<sup>2+</sup> ions, respectively [Figures 1-3].

Furthermore, the same manner of Pt<sup>2+</sup> ion shown in Figures 4 and 5 was used to obtain the calibration graph of Pt<sup>2+</sup>, Ir<sup>2+</sup>, Y<sup>2+</sup>, and V<sup>2+</sup> ions. The calibration graphs were found in the range of (0.3–1.5), (1–5), (1.5–6.0), and (1–5) µg/ml (*n* = 3) for La<sup>3+</sup>, Eu<sup>2+</sup>, Er<sup>2+</sup>, and Lu<sup>2+</sup> ions, respectively.

## DISCUSSION OF THE METHOD

In this experiment, Lanthanide ions can be separated by applying complexometric ions simultaneous exchange technique<sup>[23]</sup> and thus the d-orbital or f-orbital were dissociated by complexing with reagents, this experiment can be achieved by the Chromatography separation technique, therefore, it is possible to take advantage of the differences in complexity of elements between groups (f and d). Lanthanide elements and transition ions become making have stable selectivity elements into the form complexes within 18-Crown-6-Ether and Methane sulfonic acid as Eluent that allowing with separation of transition ions while Lanthanide elements are remained non-separated in the column, after a period of time the lanthanides are separated.<sup>[24-26]</sup> Elements (f and d) are about 36–38 min and that lanthanide elements can be detected by measuring absorption at 350 nm on forming an 18-crown-6-ether complex. The size of ions is important in determining when this elution occurs for the smaller and larger ions.<sup>[27]</sup>

A clear explanation can be found for estimating the M: L ratios by the method of the known molecular percentage in analytical chemistry,<sup>[28,29]</sup> where the ratio of M: L to the complex formed between the metallic ions interacting with oxalic acid was found to be 1:2 or 1:3 from M: L ratios, which sets the metal ions to move to the formation of more stable complexes with ligand 18-crown-6-ether which are deposited more stable.<sup>[30,31]</sup> Clearly, the KSP (Constant solubility) values measured for the complex formed between metallic

ions with oxalic acid are much lower than the KSP values of the complex formed between the metal ions with 18-crown-6-ether.<sup>[32,33]</sup> In the acidic media at pH 3, the OH groups in the acid are released to release molecules of water, thus creating the electronic couplings on the oxygen atoms of the hydroxyl group in the acid to bind with the metal ions in the lanthanides and the ions of the transition elements. However, the bonding process is less stable than if it was associated with six oxygen atoms, all steps of the work were done in 25°C.<sup>[34-36]</sup>

## Lower Limits of Detection (LLOD) and Quantitation

The LLOD and LLO quantitation (LLOQ) are the concentrations that give signal-to-noise ratio of 3:1 or 10:1, respectively, which can be detected and verified by the relation of standard deviation of response (SD) to the slope of calibration curves (S):<sup>[37]</sup>

$$\text{LLOD} = 3.3 \text{ SD/S}, \text{ LLOQ} = 10 \text{ SD/S}$$

All peaks were well resolved and the precision was acceptable. System suitability of the method was studied through method development by calculating LOD, LOQ, intercept, slope, retention time, standard error, standard error estimate, and repeatability favorable for the system are summarized in Tables 1-3. The values in Table 3 referred to high accuracy and success method project.

## Linearity and Range<sup>[38]</sup>

The linearity of the method was tested to demonstrate a proportional relationship of response versus analytes concentration. It was studied at five concentration levels in the range of 0.5–1.0 µg ml<sup>-1</sup> (*n* = 3) for lanthanide ions and the five concentration levels in the range of 0.3–6 µg ml<sup>-1</sup> (*n* = 3) for transient metals. The regression equation was found linear by plotting peaks height verses lanthanides concentration, correlation coefficient obtained for the lanthanides and transient metals obtained for the regression line were greater than 0.9971–0.9997 for lanthanide ions and 0.9971–1.0 for transient metals that shown in Tables 2 and 3 represents the regression data including correlation coefficient, slope, intercept, standard error, and standard error estimate.

## Accuracy/Recovery Studies<sup>[39]</sup>

The accuracy of an analytical method is determined by how

**Table 2:** Accounts of intercept and slope using five concentrations (*n*=3) against peaks height for each ion

Ions	Retention time (min)	R <sup>2</sup>	Standard error <sup>a</sup>	Standard error estimate <sup>b</sup>	Intercept	Slope	LOD µg mL <sup>-1</sup>	LOQ µg mL <sup>-1</sup>
La <sup>3+</sup>	26	1	0	0	3	10	2.608	7.906
Eu <sup>2+</sup>	28	9997	0.172	0.183	2.5	15	2.059	5.589
Er <sup>3+</sup>	33	0.9989	0.184	0.196	5	12	0.1002	6.69
Lu <sup>3+</sup>	38	0.9971	0.825	0.916	4	11	0.0672	5.654

<sup>a</sup>standard error, <sup>b</sup>standard error estimate, LOD: Limit of detection, LOQ: Limit of quantitation

**Table 3:** Regression statistics of the proposed method with LOD, LOQ, intercept, and slope for transient metals will coelute with the lanthanides

LOQ $\mu\text{g ml}^{-1}$	LOD $\mu\text{g ml}^{-1}$	Slope	Intercept	Standard error estimate <sup>b</sup>	Standard error <sup>a</sup>	R <sup>2</sup>	Retention time (min)	Ions
7.906	2.608	10	3	0	0	1	26	La <sup>3+</sup>
5.589	2.059	15	2.5	0.183	0.172	0.9997	28	Eu <sup>2+</sup>
6.69	0.1002	12	5	0.196	0.184	0.9989	33	Er <sup>3+</sup>
5.654	0.0672	11	4	0.916	0.825	0.9971	38	Lu <sup>3+</sup>
4.75	0.567	34.667	0.6	1.032	1.083	0.9971	10	Pt <sup>2+</sup>
4.995	0.425	30	0.5	1.621	1.532	0.9979	12	Ir <sup>2+</sup>
0.3874	0.622	26	6.36E-15	0	0	1	11	Y <sup>2+</sup>
0.1034	0.428	19	0.033	0.008	0.007	0.9999	14	V <sup>2+</sup>

LOD: Lower limit of detection, LOQ: Limit of quantitation

**Table 4:** Method accuracy from recovery assays for the studied analyses

Ions	Recovered conc.	Recovery %	RSD %
La <sup>3+</sup>	1.50	93	0.439
Eu <sup>2+</sup>	0.60	96	0.494
Er <sup>3+</sup>	0.60	100	0.596
Lu <sup>3+</sup>	1.50	98	0.522
Pt <sup>2+</sup>	0.90	97	0.517
Ir <sup>2+</sup>	3.00	96	0.488
Y <sup>2+</sup>	4.50	97	0.479
V <sup>2+</sup>	3.00	93	0.500

RSD: Relative standard deviation

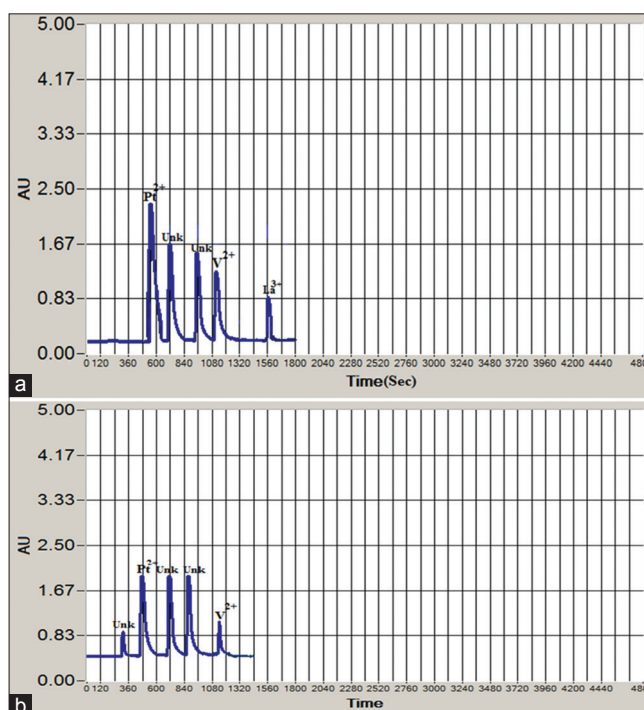
close the test results obtained by that method come to the true value. It can be determined by recovery studies, where a known amount of standard is spiked in the sample to be analyzed. The results of accuracy studies are shown in Table 4 and it is evident that the method is accurate within the desired range.

### Precision<sup>[40,41]</sup>

The precision of method, reported as %RSD, was estimated by measuring repeatability (intraday assay) on three replicate injection for the intermediate concentration of each ion ( $n = 3$ ), shown in Table 4, and intermediate precision (interday variation) was studied for 2 days for the intermediate concentration of each ion ( $n = 3$ ). All the results are given in Table 5.

### Applications

A number of applications were carried out using the developed method of detecting and estimating transitional elements and lanthanide ions. These elements were discovered in the artesian wells close to sea water [Figures 7a-b) and the artesian wells in the desert of the Iraqi city of Ramadi [Figures 8a-b).



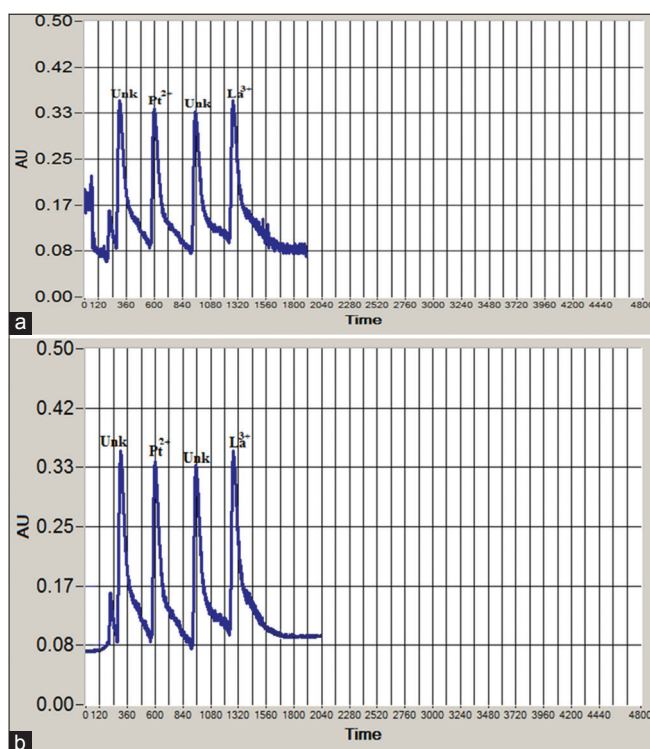
**Figure 7:** (a) Determination of ionic complexes in water wells artesian in Seawater, except column, Dionex IonPac CS18 with Guard column GS18; wavelength 350 nm; eluent, 0.16 mM methane sulfonic acid; injection volume, 100  $\mu\text{L}$ ; solutes, Pt<sup>2+</sup>, V<sup>2+</sup>, and La<sup>3+</sup> (b) Determination of ionic complexes in water wells artesian in Seawater, except column, Dionex IonPac CS18 without Guard column; wavelength 350 nm; eluent, 0.16 mM methane sulfonic acid; injection volume, 100  $\mu\text{L}$ ; solutes, Pt<sup>2+</sup> and V<sup>2+</sup>

## CONCLUSION

The above eight ions are measured at 350 nm using 18-crown-6-ether as the post-column derivatizing reagent. A simple, rapid, accurate, precise, low cost, and least time-consuming high-performance liquid chromatography (HPLC) method for the quantitative analysis of the lanthanide metals in standard solution has been developed and validated. The intrarun

**Table 5:** Intra- and inter-day precision and accuracy of analytes

Ions	Intraday			Interday		
	Found	%Rec	%RSD	Found	%Rec	%RSD
La <sup>3+</sup>	1.4	93	0.439	1.43	95	0.6
Eu <sup>2+</sup>	0.58	96	0.494	0.57	95	0.439
Er <sup>3+</sup>	0.6	100	0.596	0.59	98	0.596
Lu <sup>3+</sup>	1.48	98	0.522	1.48	98	0.522
Pt <sup>2+</sup>	0.88	97	0.517	0.88	100	0.517
Ir <sup>2+</sup>	2.9	96	0.488	2.8	93	0.488
Y <sup>2+</sup>	4.4	97	0.479	4.3	95	0.479
V <sup>2+</sup>	2.8	93	0.5	2.8	100	0.502



**Figure 8:** (a) Determination of ionic complexes in water wells artesian in the desert of the Iraqi city of Ramadi, except column, Dionex IonPac CS18 without Guard column; wavelength 350 nm; eluent, 0.16 mM methane sulfonic acid; injection volume, 100  $\mu$ L; solutes, Pt<sup>2+</sup> and La<sup>3+</sup> (b) Determination of ionic complexes in water wells artesian in the desert of the Iraqi city of Ramadi, except column, Dionex IonPac CS18 with Guard column GS18; wavelength 350 nm; eluent, 0.16 mM methane sulfonic acid; injection volume, 100  $\mu$ L; solutes, Pt<sup>2+</sup> and La<sup>3+</sup>

and inter-run variability and accuracy results were found in acceptable limits. The simplicity of the method, shorter run time, economical nature, and low limits of detection and quantitation make the method superior to the other reported HPLC methods. The method could be applied to the analysis of studied inorganic materials. The method has been applied to the study cations metal interactions and the results reveal that the presence of metals ion has a more pronounced effect on the availability of cations and complexion is the main

factor responsible for decreased or increased availability of cation. Therefore, a concomitant administration of transient metals with lanthanide seems advisable. Moreover, a proper time interval should be maintained.

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## REFERENCES

- Rajendran M, Yapici E, Miller LW. Lanthanide-based imaging of protein-protein interactions in live cells. *Inorg Chem* 2014;53:1839-53.
- Guillen O, Daiguebonne C, Calvez G, Bernot K. A long journey in lanthanide chemistry: From fundamental crystallogenes studies to commercial anticounterfeiting taggants. *Acc Chem Res* 2016;49:844-56.
- Riri M, Hor M, Kamal O, Eljaddi T, Benjjar A, Hlaïbi M. New gadolinium (III) complexes with simple organic acids (Oxalic, Glycolic and Malic Acid). *J Mater Environ Sci* 2011;2:303-8.
- Sinha SP. *Complexes of Rare Earths*. 1<sup>st</sup> ed. Oxford: Pergamon Press; 1966.
- Pilipenko AT, Tanaiko MM. *Applications of mixed-ligand complexes in analytical chemistry (1966-1972)*. *Talanta* 1974;21:501-11.
- Butts WC, Banks CV. Solvent extraction and gas chromatography of the rare earth mixed-ligand complexes of hexa-fluoroacetylacetone and tributyl phosphate. 1970;42:133-6.
- Zhenbo MA, Boulton B. *Supramolecular medicinal chemistry: Mixed-ligand coordination complexes*. *Mol Pharm* 2007;4:373-85.
- Dietrich B, Hosseini MW, Lehn JM, Sessions RB. Anion receptor molecules. *Synthesis and anion-binding*

- properties of polyammonium macrocycles. *J Am Chem Soc* 1981;10:1282-3.
9. AL-Sowdani KH, Al-Salman HNK. Determination of some cations using A homemade ion chromatography system. The first scientific conference the college of education for pure sciences; 2012.
  10. AL-Sowdani KH, Al-Salman HNK, AL-Jadaan SN. Construction of a homemade ion chromatography system to determination anions and cations. *Iraqi Patented*, 181(4333); 2015.
  11. AL-Sowdani KH, Al-Salman HNK, AL-Jadaan SN. Semi-automated home-made Ion Chromatography System Supplied with UV-Vis detector for determination of Pharmaceutical preparations and Organic compounds. *Iraqi Patented*, 503(5714); 2019.
  12. Roy S, Chakraborty A, Maji TK. Recent advances in complex functional materials: From design to application. *Coord Chem Rev* 2014;273:139-64.
  13. Benelli C, Gottschee D. Introduction to molecular magnetism: From transition metals to lanthanides. Weinheim: Wiley; 2015.
  14. Höller CJ, Müller-Buschbaum K. The first dinitrile frameworks of the rare earth elements: Infinity(3) [LnCl<sub>3</sub>(1,4-ph(CN)<sub>2</sub>)] and infinity(3)[Ln<sub>2</sub>Cl<sub>6</sub>(1,4-ph(CN)<sub>2</sub>)], Ln = sm, gd, tb, Y; access to novel metal-organic frameworks by solvent free synthesis in molten 1,4-benzodinitrile. *Inorg Chem* 2008;47:10141-9.
  15. Daignebonne C, Kerbellec N, Bernot K, Gérault Y, Deluzet A, Guillou O, *et al.* Synthesis, crystal structure, and porosity estimation of hydrated erbium terephthalate coordination polymers. *Inorg Chem* 2006;45:5399-406.
  16. Remy MK, Wankasi VD, Dikio ED. Morphology and adsorption of chromium ion on uranium 1, 2, 4, 5-benzenetetracarboxylic acid metal organic framework (MOF). *Hem Ind* 2016;70:565-72.
  17. Nayuk R, Zacher D, Schweins R, Wiktor C, Fischer RA, Tendeloo G, *et al.* modulated formation of MOF-5 nanoparticles-A SANS analysis. *J Phys Chem C* 2012;116:6127-35.
  18. Calvez G, Daignebonne C, Guillou O. Unprecedented lanthanide-containing coordination polymers constructed from hexanuclear molecular building blocks: {[Ln<sub>6</sub>O(OH)<sub>8</sub>](NO<sub>3</sub>)<sub>2</sub>(bdc)(Hbdc)·2NO<sub>3</sub>·H<sub>2</sub>O)}<sub>n</sub>. *Inorg Chem* 2011;50:2851-8.
  19. Dasgupta R, Seibt F. Examining cholinergic synaptic signaling in the thalamic reticular nucleus. *J Clust Sci* 2017;22:279-88.
  20. Guillerm V, Weseliński Ł, Belmabkhout Y, Cairns AJ, D'Elia V, Wojtas Ł, *et al.* Discovery and introduction of a (3, 18)-connected net as an ideal blueprint for the design of metal-organic frameworks. *Nat Chem* 2014;6:673-80.
  21. Alezi D, Peedikakkal AM, Weselinski L, Guillerm V, Belmabkhout Y, Cairns AJ, *et al.* Functional materials design, discovery development. *J Am Chem Soc* 2015;137:5421-30.
  22. Luebke R, Belmabkhout Y, Weselinski L, Cairns AJ, Alkordi M, Norton G, *et al.* Versatile rare earth hexanuclear clusters for the design and synthesis of highly-connected fw-MOFs. *Chem Sci* 2015;6:4095-102.
  23. Nugent P, Belmabkhout Y, Burd SD, Cairns AJ, Luebke R, Forrest K, *et al.* Porous materials with optimal adsorption thermodynamics and kinetics for CO<sub>2</sub> separation. *Nature* 2013;495:80-4.
  24. Xue DX, Cairns AJ, Belmabkhout Y, Wojtas L, Liu Y, Alkordi MH, *et al.* Tunable rare-earth fcu-MOFs: A platform for systematic enhancement of CO<sub>2</sub> adsorption energetics and uptake. *J Am Chem Soc* 2013;135:7660-7.
  25. Ding YS, Chilton NF, Windemere R, Zheng YZ. On approaching the limit of molecular magnetic anisotropy: A near-perfect pentagonal bipyramidal dysprosium (III) single-molecule magnet. *Angew Chem* 2016;128:16305-8.
  26. Calvez G, Natur FL, Daignebonne C, Bernot K, Suffren Y, Guillou O. Lanthanide-based hexa-nuclear complexes and their use as molecular precursors. *Coord Chem Rev* 2017;340:134-53.
  27. Guillou O, Guillou C, Daignebonne G, Calvez K, Bernot C, Daignebonne G, *et al.* A long journey in lanthanide chemistry: From fundamental crystallogensis studies to commercial anti-counterfeiting taggants. *Acc Chem Res* 2016;49:844-56.
  28. Langley SK, Chilton NF, Gass IA, Moubaraki B, Murray KS. Molecular coolers: The case for [Cu II 5 Gd III 4]. *Chem Sci* 2011;2:1166-9.
  29. Gregson M, Chilton NF, Ariciu AM, Tuna F, Crowe IF, Lewis W, *et al.* A monometallic lanthanide bis (methanediide) single molecule magnet with a large energy barrier and complex spin relaxation behavior. *Chem Sci* 2016;7:155-65.
  30. Chilton NF, Goodwin CA, Mills DP, Winpenny RE. The first near-linear bis (amide) f-block complex: A blueprint for a high temperature single molecule magnet. *Chem Commun* 2015;51:101-3.
  31. Jagadish B, Guntle GP, Zhao D, Gokhale V, Raghunand N. Redox-active magnetic resonance imaging contrast agents: Studies with thiol-bearing 1, 4, 7, 10-tetraazacyclododecane-1, 4, 7, 10-tetracetic acid derivatives. *J Med Chem* 2012;55:10378-86.
  32. Banerjee SR, Pullambhatla M, Foss CA, Nimmagadda S, Ferdani R, Anderson CJ, *et al.* Cu-labeled inhibitors of prostate-specific membrane antigen for PET imaging of prostate. *J Med Chem* 2014;57:2657-69.
  33. Kiefer GE, Jurek P, Ferreira CL, Benard F, Guerin B. Evaluation of 64-Cu-labeled bifunctional chelate-bombesin conjugates. *Bioconjug Chem* 2011;22:1729-35.
  34. Price EW, Cawthray JF, Bailey GA, Ferreira CL, Boros E, Adam MJ, *et al.* H4octapa: An acyclic chelator for 111In radiopharmaceuticals. *J Am Chem Soc* 2012;134:8670-83.
  35. Borsig N, Scheinost AC, Shaw S, Schild D, Neumann T. Uptake mechanisms of selenium oxyanions during the ferrihydrite-hematite recrystallization. *Geochim Cosmochim Acta* 2017;206:236-53.



36. Hennig C, Ikeda-Ohno A, Kraus W, Weiss S, Pattison P, Emerich H, *et al.* Crystal structure and solution species of ce(III) and ce(IV) formates: From mononuclear to hexanuclear complexes. *Inorg Chem* 2013;52:11734-43.
37. Mitchell KJ, Abboud KA, Christou G. Atomically-precise colloidal nanoparticles of cerium dioxide. *J Phys Chem C* 2017;1445:5810-8.
38. Fan L, Wang C, Chen M, Zhu B. Recent development of ceria-based nano-composite materials for low temperature ceramic fuel cells and electrolyte-free fuel cells. *J Power Source* 2013;234:154-74.
39. Sun C, Li H, Chen L. Nanostructured ceria-based materials: Synthesis, properties and application. *Energy Environ Sci* 2012;5:8475-505.
40. Luebke R, Eubank JF, Cairns AJ, Belmabkhout Y, Wojtas L, Eddaoudi M. The unique rht platform, ideal for pinpointing the functionalization and CO<sub>2</sub> adsorption relationship. *Chem Commun* 2012;48:1455-7.
41. Bernot X, Yi K, Pointillart F, Poneti G, Calvez G, Daignebonne C, *et al.* A luminescent and sublimable dye III-based single-molecule magnet. *Chem Eur J* 2012;18:11379-87.

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## SUPPLEMENTARY MATERIAL

1. Additional file.
2. Figures of chemical linking between complexes with stationary phases used in high-performance liquid chromatography separation.

### 1-ADDITIONAL FILE

1. In the moderate and alkaline acid circles, the hydrogen bond can break down as the functional groups of carboxylic and phosphoric groups become more ionized. These ionized groups, together with electronic oxygen atoms in these groups, contribute to the formation of ionic bonds and covalent bonds with the studied ions.

We observe from Figure 1 that there is a possibility of ionizing only a carboxylic functional group because the ionization of the other group inhibits this ionization. This phenomenon is specific to polymeric compounds containing functional groups.

2. In strong acidic circles, the nature of the correlation is purely correlated so that the phosphorus groups cannot enter in connection due to the presence of the internal hydrogen bond which pulls the electronic cloud from OH toward.  $P=O$  shows in Figure 2.

Based on the above, we can say that in the acidic circles  $pH \leq 3$ , there are very strong complexes with common symbiotic bonds. This contributes to the formation of the free electrons on the oxygen atoms of the two carboxylic and phosphoric groups, whereas the contribution of the ionic bond may be non-existent. A compound that affects the amount of polarization of the functional groups so as to provide an equal distribution of the electronic density between the atoms that bind them. This means that the probability of these groups is lower or

supported with transitional metal ions. In this medium, we can expect a contribution of ionic bonding to about 5%. This association only contributes to carboxylic groups. In weak acidic environments,  $pH \geq 5$  is formed with strong bonds with common symbiotic bonds with weak ionic bond contribution. This increases the number of ionized functional groups, and therefore, we expect ionic properties to prevail in the alkaline environment with a weaker contribution to the common symbiotic association.

Figure 2 shows that polymer is a multinucleus complex and we expect it to form a multicore complex with multicore electrolytes with studied electrolytes. This will not occur due to the spatial disability of functional groups, which is not allowed to contribute with more than metal scraps, rotation around itself, bending.

### 2-FIGURES OF CHEMICAL LINKING BETWEEN COMPLEXES WITH STATIONARY PHASES USED IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY SEPARATION

- 1- Figure 1. Chemical Structure of a possibility ionizing for only a carboxylic functional groups.
- 2- Figure 2. Chemical Structure of a possibility ionizing for a carboxylic functional and phosphoric groups.

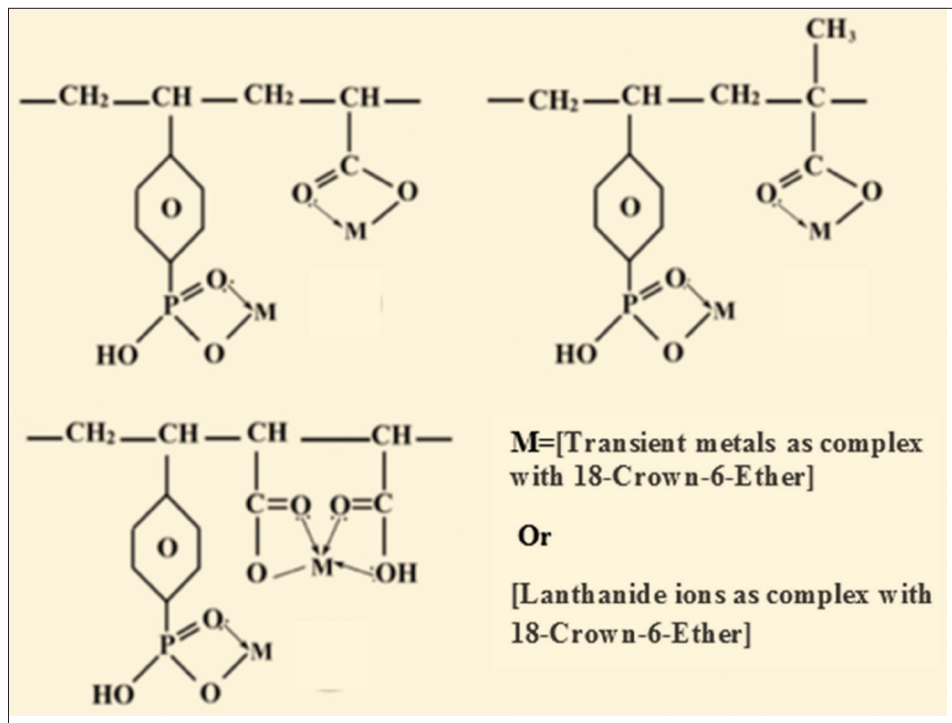


Figure 1: Chemical structure of a possibility ionizing for only a carboxylic functional groups

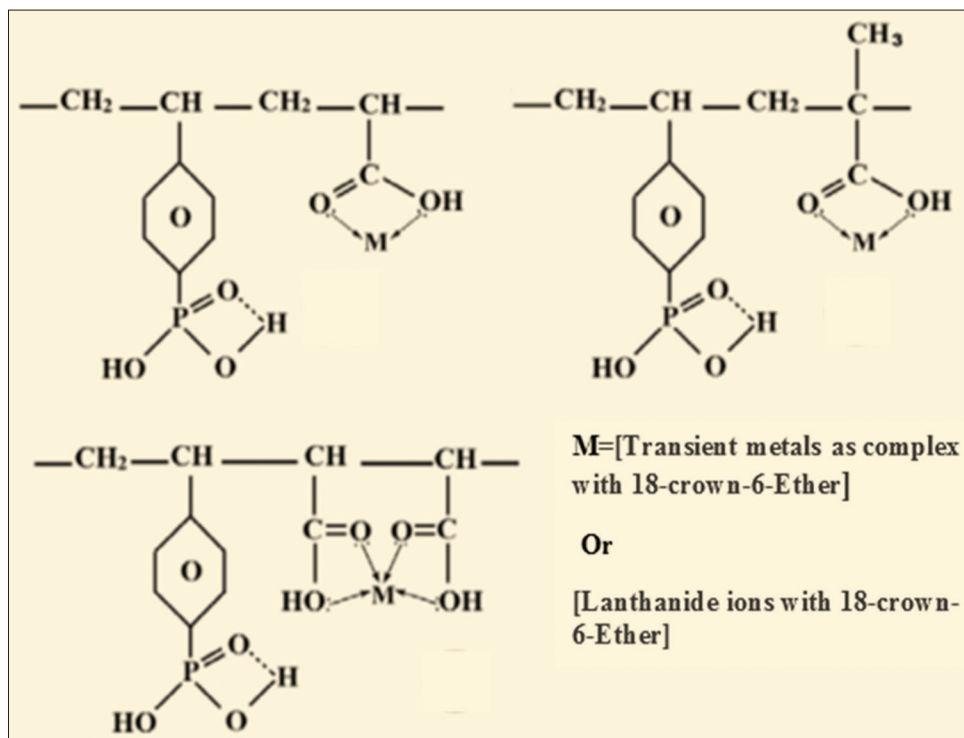


Figure 2: Chemical structure of a possibility ionizing for carboxylic functional and phosphoric groups