



## Derivative Spectrophotometric Determination of Lu, Tb and Tm Using Fluorescein Dye

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*In Loving Memory of Late Professor Doctor "Mohamed Refaat Hussein Mahran"*

### Abstract

The most straightforward technique to boost selectivity is to derivatively modify the spectrum; this process can be used to eliminate spectral interference, which in turn raises the assay's selection. Digital data derivatization is a well-known technique for separating valuable signals from noisy data, and it has been observed that the first derivative increases selectivity when first, second, third, and fourth derivatives are tested, from this point the research study is considered by the utilization of first order derivative spectrophotometry for the simultaneous determination of lutetium, terbium and thallium rare earth elements without extraction or separation. The developed procedure is simple, reliable and sensitive. This method allows the determination of lutetium and terbium in a sample of phosphate rock. Optimum factors affecting the formation and measuring of the complexes such as wavelength, pH, initial dye concentration, molar ratio and linear calibration graphs in the range 0.25 to 12  $\mu\text{g}^{-1}$  for Lu and Tb was obtained whereas relative standard deviation RSD% was 1.75 and 1.58 and percentage error 1.01 % and 0.91 % respectively.

Keywords: derivative, Lu, Tb, Tm and fluorescein dye.

### 1. Introduction

Due to physical and chemical similarities of REE make their determination usually difficult and complicated. This is particularly true if a selected element among them has to be determined in the mixture of the other REE, because of numerous interferences and coincidences [1]. The rare earth elements make up the lanthanide series which, in spite of their scarcity and the fact that they are difficult to obtain, are highly valued for their unique and unrivalled spectroscopic properties [2]. Rare earth elements of high purity play a significant role in many areas of contemporary techniques. They also have many scientific applications. For example, their compounds are used as catalysts in the production of petroleum and synthetic products, lanthanides are used in lamps, lasers, magnets, phosphors, motion picture projectors, and X-ray intensifying screens. The addition of the pyrophoric mixed rare-earth alloy called Mischmetal or lanthanide silicates improves the strength and workability of low alloy steels. Therefore, the preparation of high purity rare earth elements is very important for such technologies [3]. The second derivative spectrophotometric method has been developed as a procedure for the determination of neodymium, holmium and erbium in mixed rare earths. It was found that the 1-ethyl-6,

8-difluoro - 7 - (3-methyl-1-piperaziny)-4-oxo-1,4-dihydro-3-quinoline carboxylic acid forms stable complexes with neodymium, holmium and erbium ions in the pH 9.2-10.5 range [4]. Surface-enhanced laser-induced breakdown spectroscopy (SENLIBS) was applied to determine the REEs (La, Ce, Pr, and Nd) in an aqueous solution, in this method, the analytical solution was converted from liquid to solid, which could overcome the problems from directly analyze of liquid sample. The quantitative determination of La, Ce, Pr, and Nd elements were successfully carried out. [5]. Using phenyl tripeora acetone; Nd, Ho, Er, and Tm were determined using second and third order derivative spectrophotometry. Reviewing recent uses of derivative spectrophotometry and development directions is presented by [6]. Derivative UV-spectrophotometry is an analytical technique of enormous implication commonly in obtaining mutually qualitative and quantitative in order from spectra that are of unresolved bands, with respect to qualitative and quantitative analysis, it uses first or higher derivatives of absorbance in accordance with wavelength [7,8]. Derivative spectrophotometry is an analytical technique of great utility for extracting both qualitative and quantitative information from spectra composed of unresolved bands (which are generated from parent zero-order ones), and for

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Receive Date: 27 November 2023, Revise Date: 08 January 2024, Accept Date: 10 January 2024

DOI: 10.21608/ejchem.2024.251292.8920

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eliminating the effect of baseline shifts and baseline tilts. derivative treatment continues to be a promising tool for Multi-component Determination, Kinetic Studies, Pharmaceutical, clinical Analysis,

Environmental fields of analysis or Food Analysis as it provides selective, validated, simple and cost-effective analytical method [9]. The analytic forms of the principal Hugoniots of actinium (Ac) and the lanthanide promethium (Pm), which have both never been measured or calculated before, as well as those of terbium (Tb), thulium (Tm), and lutetium (Lu), the three least studied of the remaining lanthanides. They are based on our new analytic model of principal Hugoniots. A comparison of the five Hugoniots to our own independent theoretical calculations demonstrates very good agreement in every case [10].

The current work examined the detection of lutetium, terbium, and thulium in ores using fluorescein dye using a sensitive and selective derivative spectrophotometric approach. Optimal wavelength, pH, dye concentration, duration time, molar ratios, and calibration curves were among the optimal factors influencing the complex formation and measurement that were examined.

## 2. Experimental

### 2.1. Instrumentation

A Shimadzu (UV-11601) double beam UV-visible spectrophotometer with wavelength accuracy of  $\pm 0.5$  nm and ranges of 190 to 1100 nm.

Three buffer solutions, 4, 7, and 10, were used to calibrate the pH meter, NEL 980.

### 2.2. Chemicals

Double-distilled water was used for all solutions, and analytical grade chemical reagents were employed throughout the experiments.

Hydrochloric, sulphoric, nitric, perchloric and formic acids, potassium hydroxide, fluorescein dye, cetylpyridinium chloride (Sigma-Aldrich), standard solutions 1000 ppm Lu, Tb and Tm (Fluka).

In a 100 ml volumetric flask, 0.0328 g of fluorescein dye was dissolved with double distilled water to create a  $10^{-3}$  M dye solution, which was then finished as directed.

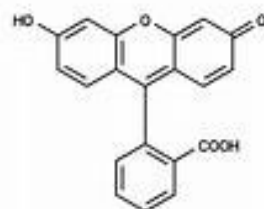
In a 100 ml volumetric flask, 0.2 g of cetylpyridinium chloride (CPC) was dissolved in doubly distilled water to create a cetylpyridinium chloride (CPC) solution  $10^{-3}$  M. The process was carried out to the correct concentration of 0.2%.

In a 100 ml volumetric flask with double distilled water, 25.88 ml (0.1M) of formic acid and 9.65 ml (0.1M) of potassium hydroxide were combined to provide the buffer solution for the HCl medium. The mixture was then finished to the mark.

## 3. Results and Discussions

### 3.1. Characteristics of The Used Dye

The used dye, namely fluorescein dye (organic dye), has chemical formula ( $C_{20}H_{12}O_5$ ) and has the following structural formula:



And it is available in a dark orange/red powder that is slightly soluble in both water and alcohol, it possesses several favorable properties, including high molar absorptivity, selectivity of the complex formations with metal ions, and stable complex formation constants with metal ions [11]. There are multiple functional groups, including carboxylate and hydroxide, that can form a complex with lutetium, terbium, and thulium, as can be seen from the structural formula of the dye under study.

### 3.2. Spectrum of Fluorescein Dye and Complexes

The fluorescein dye's absorption spectrum was measured using water as a blank. The visible regions between 350 and 550 nm in figure (1) show both the fluorescein dye's absorption spectrum and the absorption spectra of the dye complexes Lu, Tb, and Tm. After examining the data, it was discovered that the dye's maximum absorbance value was 494 nm, while the three complexes' maximum absorbance value was 436 nm.

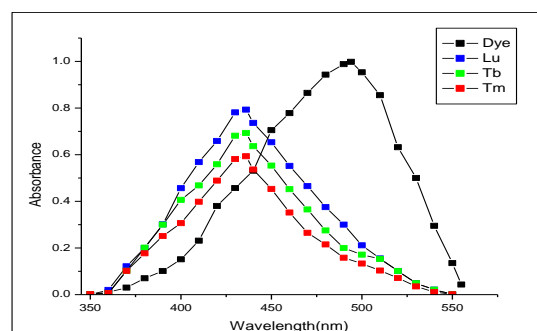


Fig. (1). Dyes' absorption spectra against water and complexes of Lu, Tb, and Tm against reagent blank

### 3.3. Influence of Various Acidic Media on The Fluorescein Dye Complexes of Lu, Tb, and Tm

Different concentrations from perchloric, hydrochloric, nitric and sulfuric acids were studied in order to examine the impact of these acid media

concentrations (pH) on complex formation. An aliquot of 1 ml from each of Lu, Tb, and Tm ( $10^{-3}$  M) and 1 ml fluorescein dye ( $10^{-3}$  M) were kept constant in a 10 ml volumetric flask along with various pH concentrations from stock acid solution 1,  $10^{-2}$ , and  $10^{-4}$  N, and the contents were completed to the mark in order to determine the ideal acidic pH medium. Between 350 and 550 nm was the measurement range for the absorbance. The data obtained regarding the impact of varying acidic media (pH values) on the complex absorbance was summarized in Tables (1, 2 and 3). The information obtained showed that complexes of Lu, Tb, and Tm formed in  $10^{-2}$  N hydrochloric acid media, with high absorbance values measured at pH 3.5.

Table (1): Influence of diverse pH ranges in diverse acidic environments on Lu complex absorbance.

pH ranges	Absorbance		
	$10^{-2}$ N HClO <sub>4</sub> media	$10^{-2}$ N HCl media	$10^{-2}$ N HNO <sub>3</sub> media
6	0.251	0.296	0.249
5.5	0.308	0.309	0.392
5	0.518	0.558	0.492
4.5	0.684	0.601	0.502
4	0.698	0.737	0.618
3.5	0.702	0.776	0.777
3	0.584	0.620	0.654
2.5	0.415	0.448	0.431

Table (2): Influence of diverse pH ranges in diverse acidic environments on Tb complex absorbance.

pH ranges	Absorbance		
	$10^{-2}$ N HClO <sub>4</sub> media	$10^{-2}$ N HCl media	$10^{-2}$ N HNO <sub>3</sub> media
6	0.319	0.396	0.242
5.5	0.508	0.409	0.328
5	0.642	0.558	0.481
4.5	0.779	0.601	0.531
4	0.742	0.737	0.670
3.5	0.864	0.854	0.723
3	0.521	0.687	0.522
2.5	0.405	0.515	0.312

### 3.4. Influence of pH Buffer for Best Creation of Lu, Tb and Tm - Fluorescein Dye Complexes

Investigating how buffer pH affects the development of metal complexes was essential. Various buffer solutions were prepared in order to investigate this impact. Using a mixture of  $10^{-2}$  N hydrochloric acid, 0.1 M formic acid, and 0.1 M potassium hydroxide buffer solutions in a way to optimum pH value studied in different media 3.5 for HClO<sub>4</sub>, HCl, and HNO<sub>3</sub> for complexes was found to

produce the best buffer having the maximum absorbance levels of the Lu, Tb, and Tm - dye complexes. The effect of pH changes on the absorbance of metal-dye complexes at their maximum wavelength,  $\lambda_{\max}$  436 nm, was summarized in table 4.

Table (3): Influence of diverse pH ranges in diverse acidic environments on Tm complex absorbance.

pH ranges	Absorbance		
	$10^{-2}$ N HClO <sub>4</sub> media	$10^{-2}$ N HCl media	$10^{-2}$ N HNO <sub>3</sub> media
6	0.193	0.296	0.201
5.5	0.344	0.409	0.320
5	0.444	0.528	0.401
4.5	0.564	0.601	0.497
4	0.617	0.637	0.570
3.5	0.687	0.701	0.687
3	0.421	0.620	0.459
2.5	0.205	0.549	0.248

Table (4): Influence of buffer pH 3.5 on the dye complexes absorbance.

Volume of buffer (ml)	Absorbance		
	Lu	Tb	Tm
0.1	0.158	0.191	0.179
0.2	0.285	0.211	0.205
0.3	0.300	0.253	0.284
0.5	0.362	0.302	0.377
0.7	0.483	0.492	0.408
1	0.512	0.592	0.517
1.5	0.346	0.480	0.422
2	0.242	0.390	0.321
2.5	0.119	0.261	0.300

### 3.5. Influence of Surfactant Concentration on The Complexes' Absorbance

Optimizing the concentration of CPC as a cationic surfactant was imperative, entailing an analysis of its impact on the molar absorptivity and sensitivity of the resultant complexes. To achieve this, a series of 10 ml volumetric flasks with fixed volumes of ( $10^{-3}$  M dye) and (Lu, Tb, or Tm) with varying volumes of ( $10^{-3}$  M CPC) solution, which was then buffered to a pH of 3.5. Double-distilled water was used to finish the last volumes of these solutions. Next, each solution's absorbance was calculated compared to a blank. According to figure (2), the maximum absorbance for all three metals was reached at  $0.5 \times 10^{-3}$  M of (CPC).

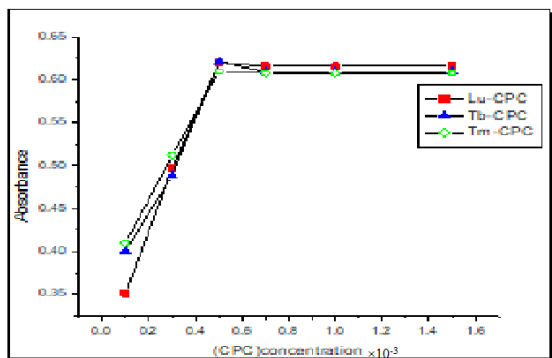


Fig (2). Influence of surfactant concentration on the complexes' absorbance.

### 3.6. Influence of Fluorescein Dye Concentration on The Complexes' Absorbance

In order to avoid deviating from Beer's law during the calibration curve construction process, the concentration of fluorescein dye should be optimized. To achieve this, a set of 10 ml volumetric flasks holding 1 ml of  $10^{-3}$ M (Lu, Tb, and Tm) with the pH adjusted to the ideal value with varying volumes of  $10^{-3}$  M fluorescein dye. After the volume was increased to 10 ml, each solution's absorbance was calculated.

According to figure (3), the complexes exhibit their maximum absorbance at a pH value of  $1 \times 10^{-3}$  M fluorescein dye concentration.

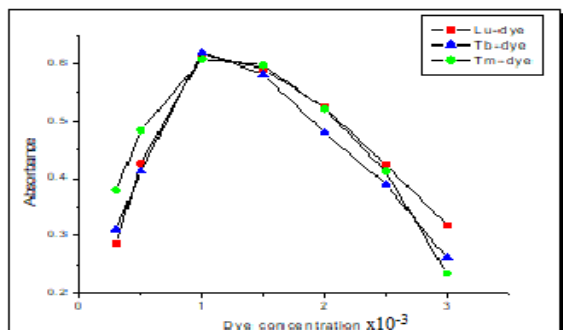


Fig (3). Influence of dye concentration on the absorbance of Lu, Tb and Tm complexes.

### 3.7. Influence of Duration Time on The Complexes' Stability

The stability of complexes for a given duration was examined after optimizing the formation of metal-dye complexes (every optimized addition was included). Both immediately and after a while, the absorbance was measured, where it was frequently measured.

It was discovered that the complexes formed immediately and remained stable for 15 min., according to the data in table (5).

Table (5): Influence of duration time on the complexes' stability.

Time (min)	Absorbance		
	Lu	Tb	Tm
Zero	0.616	0.621	0.608
3	0.620	0.621	0.610
5	0.616	0.623	0.610
7	0.620	0.622	0.608
10	0.620	0.621	0.608
15	0.616	0.621	0.610
20	0.595	0.531	0.542
25	0.521	0.494	0.462
30	0.453	0.367	0.357

#### 3.7.1. FTIR

For pure fluorescein, the FTIR spectrum show that there is wide band at  $(3400.41) \text{ cm}^{-1}$  corresponding to hydroxyl group, H-bonded-OH stretch, narrow bands at  $(1200.12) \text{ cm}^{-1}$  attributed to non-bonded hydroxyl group, OH stretch, band at  $(1605.11) \text{ cm}^{-1}$  corresponding to C-O bond and other peaks corresponding to aromatic rings. It can be observed in Fig. 4 that the main difference between fluorescein dye and its complexation with metal ions was the shift of some bands, due to an interaction with metal ions. The band belonging to O-H unit of the dye was shifted and reduced to 3450, 3500.7, and  $3500 \text{ cm}^{-1}$  for Lu, Tb, and Tm, respectively. Also, the band of carbonyl group shifted after its complexation with RE(III) to 1660, 1672.7, and  $1670.7 \text{ cm}^{-1}$  for Lu, Tb, and Tm, respectively. Hence, the binding mechanism can be considered as a complexation process between the O atoms in the fluorescein dye and studied metal ions (Scheme 1).

### 3.8. Composition of The Complex

The current study examined the dye-to-metal ratios using the continuous variation method. The molarities of the two components (metal and dye) were varied using the continuous variation method, while the total number of moles of both components remained unchanged. The metal- dye complexes had an ideal molar ratio of 1:1 from  $10^{-3}$  M dye and elements, as shown in figure 5.

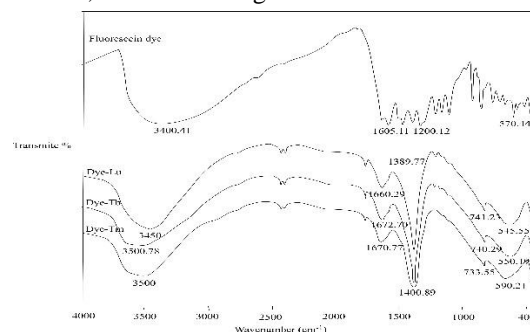
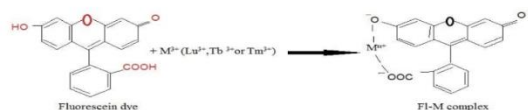


Fig. 4: FTIR spectroscopy of fluorescein dye and complexes



Scheme 1: The suggested mechanism of the complexation between fluorescein dye and studied metal ions

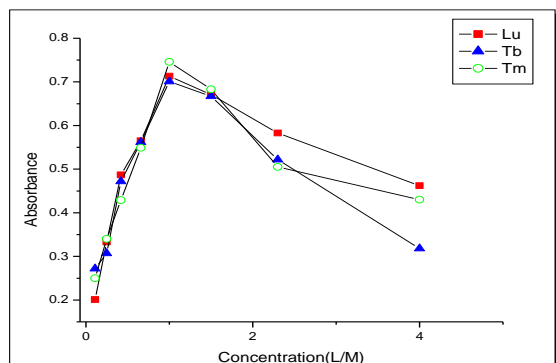


Fig (5). Continuous variation method for estimating the molar ratio between metal- dye complexes

### 3.9. Construction of Calibration Curves

It was essential to identify the concentration ranges of Lu, Tb, and Tm above or below whereby no more complexes developed, which was determined after a thorough analysis of the relevant variables affecting the fluorescein spectrophotometric determination of Lu, Tb, and Tm. By establishing calibration curves for the complexes, these two limits could be found.

As seen in figures 6, 7, and 8, the spectra provide linear calibration graphs for Lu, Tb, and Tm, respectively, in the range of 1 to 10 ppm.

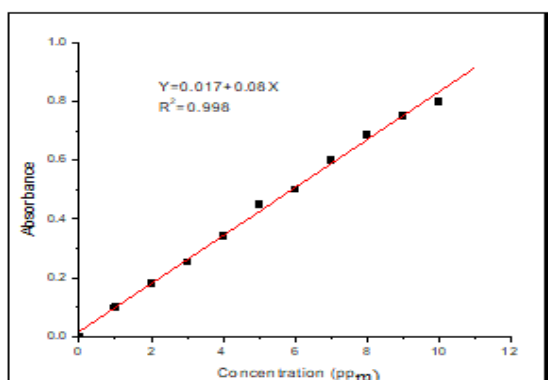


Fig (6). Calibration curve for spectrophotometric determination of Lu

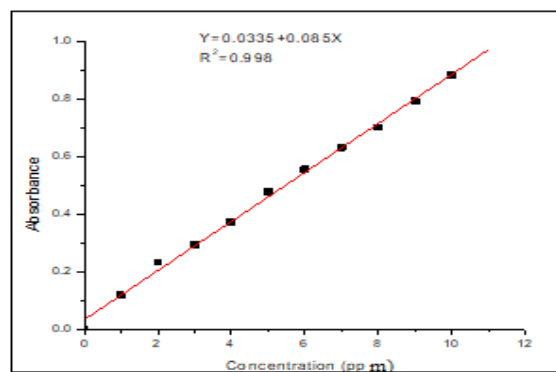


Fig (7). Calibration curve for spectrophotometric determination of Tb

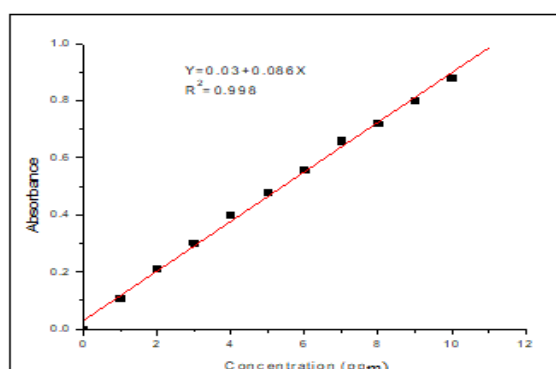


Fig (8). Calibration curve for spectrophotometric determination of Tm

### 3.10. Investigating The Interference Effect

Examining the interference effect tolerance limits of the accompanying elements with Lu, Tb, and Tm was imperative.

Table (6): Limitations of tolerance for Fe concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Fe conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.801	0.881	0.879
0.5	0.800	0.881	0.879
1	0.800	0.881	0.879
1.5	0.800	0.881	0.878
2	0.802	0.881	0.879
2.5	0.800	0.881	0.879
3	0.800	0.881	0.878
4	0.800	0.881	0.879
<b>5</b>	<b>0.988</b>	<b>0.881</b>	<b>0.879</b>
5.5	0.989	0.992	0.998
6	0.988	0.992	0.997
6.5	0.987	0.993	0.998

Table (7): Limitations of tolerance for Ca concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Ca conc. (ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.800	0.881	0.879
0.5	0.801	0.882	0.879
1	0.801	0.881	0.879
1.5	0.800	0.881	0.879
2	0.800	0.880	0.879
2.5	0.801	0.881	0.879
3	0.800	0.882	0.879
4	0.800	0.881	0.879
5	0.800	0.881	0.879
6	0.800	0.880	0.879
<b>7</b>	<b>0.999</b>	<b>0.989</b>	<b>0.998</b>
7.5	0.997	0.989	0.999
8	0.999	0.988	0.998
9	0.999	0.989	0.9

Table (8): Limitations of tolerance for Mg concentrations on the Lu, Tb and Tm- fluorescein dye complex determination

Mg conc. (ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.800	0.881	0.879
0.5	0.801	0.882	0.879
1	0.801	0.881	0.879
1.5	0.800	0.881	0.879
2	0.800	0.880	0.879
2.5	0.801	0.881	0.879
3	0.800	0.882	0.879
4	0.800	0.881	0.879
5	0.800	0.881	0.879
6	0.800	0.880	0.879
7	0.800	0.881	0.879
8	0.800	0.881	0.879
9	0.801	0.882	0.879
10	0.801	0.881	0.879
11	0.800	0.881	0.879
12	0.800	0.881	0.879
<b>13</b>	<b>0.987</b>	<b>0.999</b>	<b>0.988</b>
14	0.987	0.999	0.988
15	0.987	0.999	0.988

Table (9): Limitations of tolerance for Al concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Al conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.801	0.881	0.879
0.5	0.800	0.881	0.879

1	0.800	0.881	0.878
1.5	0.800	0.880	0.879
2	0.800	0.880	0.879
2.5	0.801	0.881	0.879
3	0.800	0.881	0.879
5	0.800	0.881	0.878
7	0.800	0.880	0.879
11	0.801	0.880	0.878
<b>13</b>	<b>0.989</b>	<b>0.997</b>	<b>0.999</b>
15	0.989	0.997	0.999
16.5	0.989	0.998	0.999
17	0.989	0.997	0.999

Table (10): Limitations of tolerance for Ti concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Ti conc. (ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.800	0.881	0.879
0.5	0.801	0.881	0.879
1	0.800	0.881	0.879
1.5	0.800	0.880	0.879
2	0.800	0.881	0.879
2.5	0.801	0.881	0.879
3	0.800	0.880	0.878
3.5	0.800	0.881	0.878
4	0.801	0.881	0.879
<b>4.5</b>	<b>0.988</b>	<b>0.993</b>	<b>0.997</b>
5	0.988	0.993	0.997
5.5	0.989	0.993	0.998
6	0.998	0.994	0.997

Table (11): Limitations of tolerance for Na and K concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Na, K conc. ppm	Absorbance					
	Na			K		
	Lu	Lu	Tb	Tb	Tm	Tm
0	0.800	0.800	0.881	0.881	0.879	0.879
0.25	0.800	0.801	0.881	0.881	0.879	0.879
0.5	0.800	0.800	0.881	0.880	0.879	0.879
1	0.801	0.800	0.881	0.881	0.879	0.878
1.5	0.800	0.800	0.882	0.880	0.879	0.879
2	0.800	0.800	0.881	0.881	0.879	0.878
2.5	0.800	0.800	0.881	0.881	0.879	0.879
<b>5</b>	<b>0.911</b>	<b>0.910</b>	<b>0.947</b>	<b>0.945</b>	<b>0.979</b>	<b>0.999</b>
7	0.911	0.910	0.947	0.945	0.979	0.999

Table (12): Limitations of tolerance for Zn concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Zn conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879

0.25	0.801	0.881	0.879
0.5	0.800	0.881	0.879
1	0.800	0.880	0.879
3	0.800	0.882	0.879
5	0.801	0.880	0.879
7	0.800	0.881	0.879
9	0.800	0.881	0.879
11	0.801	0.881	0.878
13	0.800	0.881	0.879
<b>15</b>	<b>0.997</b>	<b>0.987</b>	<b>0.999</b>
17	0.998	0.987	0.998
20	0.998	0.987	0.999

Table (13): Limitations of tolerance for Ni concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Ni conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.801	0.881	0.879
0.5	0.800	0.881	0.879
1	0.800	0.880	0.879
3	0.800	0.882	0.879
5	0.801	0.880	0.879
7	0.800	0.881	0.879
9	0.800	0.881	0.879
11	0.801	0.881	0.878
13	0.800	0.881	0.879
15	0.800	0.881	0.879
<b>17</b>	<b>0.958</b>	<b>0.987</b>	<b>0.998</b>
19	0.958	0.987	0.999
20	0.958	0.988	0.999

Table (14): Limitations of tolerance for P<sub>2</sub> O<sub>5</sub> concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

P <sub>2</sub> O <sub>5</sub> conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.801	0.881	0.879
0.5	0.800	0.881	0.879
1	0.800	0.880	0.879
1.5	0.800	0.882	0.879
2	0.801	0.880	0.879
3	0.800	0.881	0.879
4	0.800	0.881	0.879
5	0.801	0.881	0.878
<b>6</b>	<b>0.998</b>	<b>0.987</b>	<b>0.999</b>
6.5	0.997	0.987	0.999
7	0.998	0.987	0.998
8	0.998	0.987	0.999

Table (15): Limitations of tolerance for SO<sub>4</sub><sup>2-</sup> concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

SO <sub>4</sub> <sup>2-</sup> conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.1	0.800	0.881	0.879
0.3	0.801	0.880	0.879
0.5	0.801	0.880	0.879
0.7	0.800	0.881	0.878
0.9	0.800	0.881	0.879
<b>1</b>	<b>0.995</b>	<b>0.977</b>	<b>0.992</b>
2	0.995	0.977	0.992
3	0.996	0.978	0.993
4	0.995	0.977	0.992

Table (16): Limitations of tolerance for U concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

U conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.800	0.881	0.879
0.5	0.801	0.880	0.879
1	0.801	0.880	0.879
3	0.800	0.881	0.878
5	0.800	0.881	0.879
7	0.880	0.881	0.879
9	0.880	0.882	0.879
10	0.995	0.978	0.993
12	0.995	0.977	0.992
13	0.996	0.977	0.992
15	0.995	0.977	0.993

Table (17): Limitations of tolerance for Th concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Th conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.800	0.881	0.879
0.5	0.801	0.880	0.879
1	0.801	0.880	0.879
1.5	0.800	0.881	0.878
2	0.800	0.881	0.879
2.5	0.880	0.881	0.879
3	0.880	0.882	0.879
3.5	0.880	0.881	0.879
4	0.880	0.881	0.879
<b>4.5</b>	<b>0.996</b>	<b>0.977</b>	<b>0.995</b>
5	0.995	0.977	0.995
5.5	0.996	0.977	0.996
6	0.997	0.978	0.995



Table (18): Limitations of tolerance for REEs concentrations on the Lu, Tb and Tm- fluorescein dye complex determination.

Total REEs conc.(ppm)	Absorbance		
	Lu	Tb	Tm
0	0.800	0.881	0.879
0.25	0.800	0.881	0.879
0.5	0.801	0.881	0.879
1	0.800	0.880	0.879
1.5	0.800	0.880	0.879
2	0.801	0.880	0.879
2.5	0.800	0.880	0.879
3	0.800	0.881	0.879
3.5	0.801	0.881	0.879
4	0.800	0.881	0.879
4.5	0.801	0.881	0.879
<b>5</b>	<b>0.987</b>	<b>0.971</b>	<b>0.989</b>
5.5	0.987	0.971	0.989
6	0.988	0.971	0.988
7	0.987	0.972	0.988

It was evident from the interference effect study (Tables 6 to 18) above that the traditional spectrophotometry method is not suitable for determining Lu, Tb, and Tm when other elements are present. In the presence of other elements, it was discovered that the first order derivative is the most appropriate one for determining Lu, Tb, and Tm.

The interference effect of accompanying elements on the determination of Lu, Tb, and Tm with fluorescein dye was examined in accordance with the composition of the concentrates of the samples under investigation. Next, with a constant concentration of Lu, Tb, and Tm (2 ppm each), a number of established concentration mixtures of Lu, Tb, and Tm were prepared with a number of varying concentrations for each interfering element. At  $\lambda_{\max}$  436 nm, the concentrations of the Lu, Tb, and Tm standard solution only were measured under optimal conditions in comparison to the reagent blank. The same optimal conditions were used to measure the prepared solutions of Lu, Tb, and Tm (2 ppm each) with various concentrations of the interfering elements under study. The results showed that other elements mixed with Lu, Tb, and Tm should not have their tolerance concentrations exceed certain concentration values so would result in a systematic error when determining these elements using conventional spectrophotometry.

In order to attempt to counteract this interference with their accurate and precise quantitative assessment of Lu, Tb, and Tm, derivative spectrophotometry technique was found to be necessary. The most appropriate derivative, in the presence of different concentrations of accompanying interfering elements, was discovered

to be the first order derivative for the determination of Lu, Tb, and Tm-fluorescein dye complexes.

### 3.11. Opting for The Derivative Type for The Complexes' Spectrophotometric Determination

The most straightforward way to improve selectivity is through spectrum derivatization, which makes it possible to eliminate spectral interferences and raise assay selectivity as a result. Digital data derivatization is a well-known technique for separating valuable signals from noisy data, and it has been observed that employing the first derivative increases selectivity when testing the second, third, and fourth derivatives. From the first derivative spectrum (figure 9) it was found that, there are significant peaks for Lu and Tb at 350 and 410 nm respectively. From the study the applied method not applicable for the third element Tm in the present of other two elements, and it is being studied in another research.

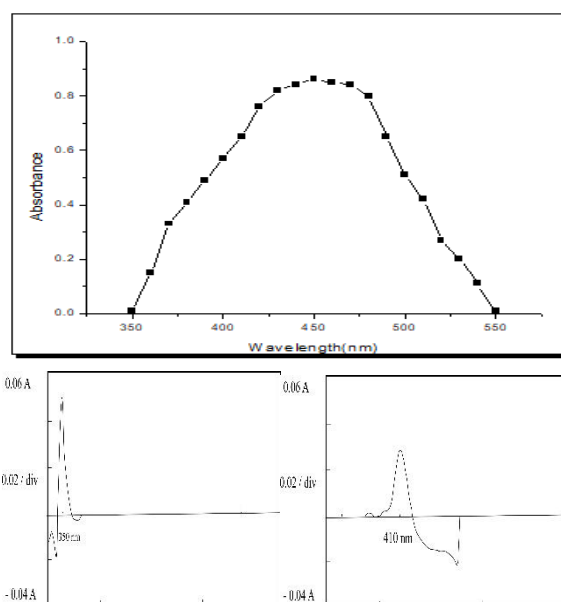


Fig (9). Absorption spectra of a mixture Lu, Tb and Tm using conventional spectrophotometry method and First derivative of Lu and Tb respectively using fluorescein dye

### 3.12. Derivative Spectrophotometric Construction of Calibration Curves

Right after an extensive investigation of the relevant variables influencing the optimal complex formation of Lu, Tb, and Tm using fluorescein dye, it became necessary to identify the optimum concentration ranges of these substances, above and below which no more complexes could form. By constructing calibration curves for the complexes, these two limits could be found. It is necessary to



perform this spectrophotometric determination within the Beer's law-compliant concentration range.

As seen in figures 10 and 11 the first derivative spectra provide linear calibration graphs for Lu, Tb, and Tm, respectively, in the range from 0.3 to 10 ppm.

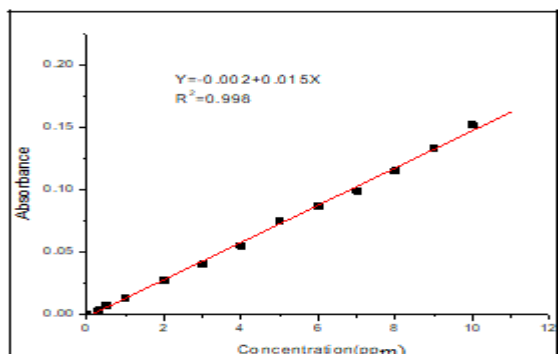


Fig (10). Calibration curve using 1<sup>st</sup>.Order spectrophotometric determination of Lu.

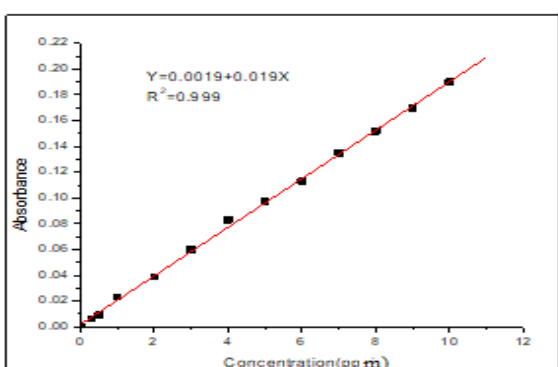


Fig (11). Calibration curve using 1<sup>st</sup>.Order spectrophotometric determination of Tb

#### 4. Application

A synthetic sample which consists only of heavy rare earth elements was created. An additional sample from the rock Abou Tartour, phosphate. The phosphate rock ore sample was accurately subjected to the method. Phosphate rock contains 1250 ppm of rare earth elements.

Solvent extraction method for rare earths from nitric acid leaching of phosphate rock using N, N, N', N'-tetraoctyl diglycol amide (TODGA) [12]. The recovery rate reached to 99.9% when a three-stage countercurrent extraction was carried out on the simulated leach solution. After that removing cerium in rare earths concentrate as it was the highest content [13]. More accurate results are obtained by separating heavy rare earth elements from other rare earth elements.

Table 13 illustrates how it's evident that the current recommended method and the ICP-OES method agree significantly.

Table (13): Analytical results of Lu and Tb (ppm) in synthetic sample and sample of phosphate rock by the currently developed approach as opposed to ICP-OES

Sample	the currently developed approach		ICP-OES method	
	Lu	Tb	Lu	Tb
Synthetic sample	2.05	2.03	2	2
Sample	0.0059	0.0068	0.0057	0.0065

JMn-1, the reference sample, was additionally examined. The outcome is shown in (table 14), where it is evident that the method's accuracy and precision are largely acceptable.

Table (14): Analytical results of Lu and Tb (ppm) in reference sample by the currently developed approach as opposed to ICP-OES

Reference sample	the currently developed approach	ICP-OES method
Lu	2	2.1
Tb	4.6	4.8

#### 5. Statistical Evaluation of The Results

It is attempted to shed some clarification on the accuracy and precision of the results obtained using the currently method through statistical analysis using appropriate statistical parameters.

##### 5.1. Standard Error

Standard error computation holds great significance in the field of applied analytical chemistry. It is employed in accordance with the subsequent equations to determine the error percentage for any developed method:

$$\text{Standard deviation (S)} = [(\sum X_1 - \bar{X})^2 / N - 1]^{1/2}$$

$$\text{Standard error (S.E.)} = S / N^{1/2}$$

$$\text{Error \%} = 100 (S.E. / \bar{X})$$

$$\text{RSD \%} = 100 (S / \bar{X})$$

Where:  $X_1$  measurement value.

$\bar{X}$  mean of the measurement values.

N number of samples (number of measurements).

synthetic sample	Conc. ppm	Mean $\bar{X}$	S	S <sup>2</sup>	SE
Lu	2.05	2.05	0.01	0.0001	0.0057
	2.04				
	2.06				
Tb	2.03	2.03	0.012	0.00013	0.0066
	2.03				
	2.05				

synthetic sample	Error %	RSD %
Lu	0.28	0.48
Tb	0.033	0.56

phosphate rock	Conc. ppb	Mean $\bar{X}$	S	S <sup>2</sup>	SE
Lu	5.77	5.79	0.1014	0.0103	0.058
	5.7				
	5.9				
Tb	6.5	6.58	0.1040	0.0108	0.060
	6.7				
	6.55				

phosphate rock	Error %	RSD %
Lu	1.01	1.75
Tb	0.91	1.58

The two elements' relative standard deviation (RSD%) attests to the high degree of accuracy attained when determining amplitude using the graphical method.

### 5.2. Sensitivity of Spectrophotometric Methods

The objective numerical expression of the sensitivity of spectrophotometric methods is the molar absorptivity ( $\epsilon$ ) at the wavelength  $\lambda_{\max}$  of the maximum absorbance of the colored species ( $\epsilon = A/c \cdot l$ ) where A is the absorbance, C the concentration of the colored species mole/l, and l the light path length. The molar absorptivity ( $\epsilon$ ) is expressed in l/mol.cm. It is convenient to express and compare the sensitivities of spectrophotometric methods in terms of specific absorptivity (a), this is obtained by ( $a = \epsilon / \text{at.wt.} \times 1000$ ), the value of (a) in ml/g.cm. The sensitivity of spectrophotometric methods is often expressed in terms of the expression (sensitivity index) given by Sandell. The sensitivity (S) according to Sandell is expressed in  $\mu\text{g}/\text{cm}^2$  and is therefore equal to ( $10^{-3}/a$ ). In analytical chemistry, the detection limit, lower limit of detection, is the lowest quantity of a substance that can be determined.

Element	Lu	Tb
( $\epsilon$ ) L/mol.cm	$30 \times 10^4$	$24 \times 10^4$
(a) ml/g.cm	1.7	1.5
(S) $\mu\text{g}/\text{cm}^2$	$5.8 \times 10^{-4}$	$6.6 \times 10^{-4}$
(Detection limit) ppm	0.1	0.1

## 6. Conclusion

The current research utilizes higher order derivative spectrophotometry to identify rare earth elements in phosphate rock samples, specifically lutetium, terbium, and thallium. Without requiring extraction or separation, these elements can be determined through the straightforward, dependable, and sensitive method. The molar ratio, wavelength, pH, initial dye concentration, and linear calibration graphs linear calibration graphs in the range  $0.25$  to  $12 \mu\text{g}^{-1}$  for Lu and Tb was obtained whereas relative standard deviation RSD% was 1.75, and 1.58 percentage error 1.01 % and 0.91 % respectively, and the molar absorptivity ( $\epsilon$ )  $30 \times 10^4$  and  $24 \times 10^4$  L/mol.cm, the specific absorptivity (a) 1.7 and 1.5 ml/g.cm, The sensitivity (S) according to Sandell  $5.8 \times 10^{-4}$  and  $6.6 \times 10^{-4} \mu\text{g}/\text{cm}^2$  for Lu and Tb respectively, and the lowest quantity of a substance that can be determined was 0.1 ppm for two elements.

In addition, the study showed that the method not applicable for the third element Tm in the present of other two elements, and it is being studied in another research.

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