

DIRECT AND DERIVATIVE SPECTROPHOTOMETRIC METHOD FOR YTTRIUM DETERMINATION IN DIFFERENT RARE EARTH CONCENTRATES

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ABSTRACT

A simple and accurate spectrophotometric method for the determination of Yttrium using xylenol orange as a chromogenic dye in different rare earth concentrates of Egyptian monazite and xenotime by using direct and derivative spectrophotometric methods was described in the present work. The calibration curve was linear from 0.2 – 6 $\mu\text{g ml}^{-1}$ at a maximum wavelength value of 568 nm. The various parameters and reaction conditions, which influence the formation of the complex, were investigated where the complex were stable for one hour. The molar absorptivity (ϵ) and Sandell's sensitivity were found to be $3.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 2.7×10^{-3} respectively. The % RSD and percentage error were 1.64% and 1.5% respectively. A high sensitivity and accuracy for the determination of yttrium in the rare earths Elements (REE) concentrates was observed when the first derivative spectrophotometric method was applied.

1. INTRODUCTION

Yttrium is an important member in the rare earths family. It is more abundant than the heavy lanthanides, resembles them in properties and occurs with them in nature. Yttrium is never found in nature as a free element hence found in three minerals bearing lanthanides; xenotime, monazite and bastnasite. It has silvery-metallic luster and spontaneously igniting in air.⁽¹⁾

Yttrium III oxide is the most important compound of yttrium it is widely used to make YVO_4 : Eu and Y_2O_3 : Eu phosphorus that give red colour of television picture tube. Y-iron garnet is very effective microwave filter, Y-aluminum garnet used as simulated diamond, Yttrium iron garnet is very efficient as an acoustic energy transmitter and transducer and cerium doped yttrium garnet crystals are used as phosphors to make white LED screens.⁽²⁾

The growing importance of yttrium in the field of nuclear chemistry and metallurgy necessitated the development of methods for the rapid determination of yttrium.⁽³⁾

A variety of methods has been used for determination yttrium these include inductively coupled plasma atomic emission

spectroscopy (ICP-AES)⁽⁴⁾, inductively coupled plasma mass spectroscopy (ICP-MS)⁽⁵⁻⁷⁾, flame atomic absorption spectrometry (FAAS)^(8,9) graphite furnace atomic absorption spectrometry⁽¹⁰⁾, X-ray fluorescence⁽³⁾.

The literature survey showed that yttrium analysis has been studied very sporadically using spectrophotometer only handful of methods were reported during the last 50 years, number of reagents has been introduced for spectrophotometric determination of yttrium among them are 2-hydroxy-1-naphthaldehyde-P-8-benzoic hydrazone (HNHBH)⁽¹¹⁾, 5,7 diiodoquinoline-8-ol and rhodamine 6G,⁽¹²⁾ bromopyrogallol red,⁽¹³⁾ arsenazo I,⁽¹⁴⁾ arsenazo (III),⁽¹⁵⁾ molybdoytric acid and basic dyes,⁽¹⁶⁾ 1-amino-4-hydroxyanthra quinon⁽¹⁷⁾ Quinalizarin green,⁽¹⁸⁾ di-2-hydroxybutric acid,⁽¹⁹⁾ chromotrope 2R,⁽²⁰⁾ ammonium purpurate,⁽²¹⁾ molybdophosphoric acid⁽²²⁾.

Xylenol orange used as indicator for determination of yttrium and rare earth elements by titration with EDTA⁽²³⁾, total RRE can be determined by xylenol orange at 600-620 nm using cetylpyridinebromide as a surfactant⁽²⁴⁾, spectrophotometric determination of yttrium-xylenol orange-EDTA complex can be extracted the complex into xylene and

determined at λ_{\max} 604 nm by shaking the solution complex with xylene⁽²⁵⁾.

In the present study, the acceptability to determine yttrium spectrophotometrically in the rare earth concentrate using xylenol orange dye was studied. Optimum factors affecting formation and measuring the complex such as maximum wavelength (λ_{\max}), pH, initial concentration of dye, molar ratio, calibration curve and interfering effect of rare earth elements were investigated. After optimizing the previous studied parameters for complex formation the method was applied for yttrium determination and applied in REE concentrates extracted from monazite and xenotime using conventional and first order derivative spectrophotometric methods.

EXPERIMENTAL

Apparatus

A UV-Visible double beam spectrophotometer model Shimadzu, 1601 equipped with 1cm cell path length used for all absorbance measurements.

A pH meter model Jenway 3510, England was applied satisfactorily in the present work and calibrated daily using two successive buffer solutions (pH 4 and 7 or 7 and 10).

REAGENTS

All the reagents used were analytical grade purity. Different concentrations of solutions were prepared from the original stock solutions 1000 $\mu\text{g ml}^{-1}$ with double distilled water.

Preparation of the dye

A 10^{-3} M of xylenol orange was prepared by dissolving 0.0168 gm with double distilled water in 25 ml volumetric flask.

Preparation of sodium acetate

A 0.2 M sodium acetate trihydrate was prepared by dissolving 2.72 gm sodium acetate trihydrate with double distilled water in 100 ml volumetric flask.

Preparation of buffer solution (Walpole buffer, pH 5)

To 14.5 ml of 0.2 M acetic acid add 35.2 ml from 0.2 M sodium acetate trihydrate and diluted to 100 ml with double distilled water

Preparation of Y and REE solutions

Stock solutions of Y and REE (1000 ppm) were used in all analyses with proper dilutions for different factors studied.

Procedure

To a standard sample solution containing not more than 2 $\mu\text{g ml}^{-1}$ of yttrium in 10 ml volumetric flask, 1.5 ml of buffer pH 5 and 0.5 ml of xylenol orange dye were added, the mixture was diluted to the mark with double distilled water and the absorbance of the complex formed was measured against a proper reagent blank at 568 nm.

RESULTS AND DISCUSSION

Several factors affecting the formation of the complex between yttrium and xylenol orange dye were studied. These parameters include maximum absorbance (λ_{\max}), pH of both the dye and yttrium dye complex, concentration of dye, buffer pH, molar ratio, duration time, calibration curve and effect of accompanying interfering ions.

Effect of pH on the absorption of xylenol orange dye

The absorption spectrum of 10^{-3} M of dye at different pH values in range from 2-7 Figure (1) indicates the maximum absorption 433at pH 3.

Effect of pH on the formation of yttrium-xylenol orange complex

The optimum pH for complex formation was studied in the range from 2-7 for this purpose 0.5 ml for yttrium ($40 \mu\text{g ml}^{-1}$), 1ml of 10^{-3} M of xylenol orange dye were mixed in 10 ml volumetric flask and the solution was completed with distilled water and the absorbance was measured. Figure (2) indicated that pH (5) gave the highest amplitude at 568

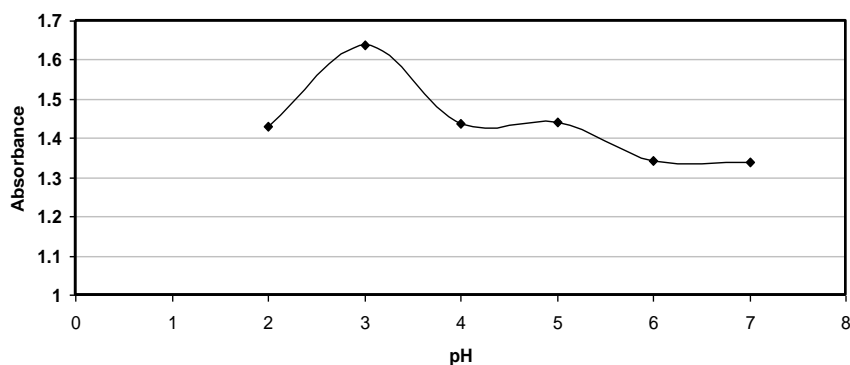
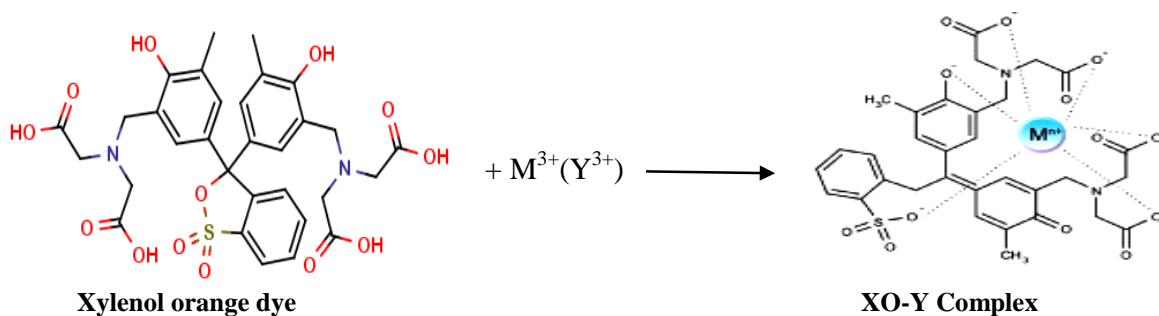


Figure (1): Effect of pH on the absorption of xylenol orange dye

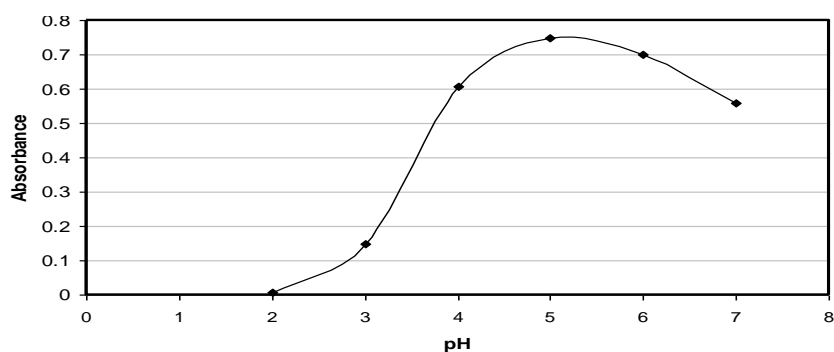


Figure (2): Effect of different pH values on Y/XO complex

nm, where it was obvious that there was a shift in wavelength from 433.5 to 568 nm.

Effect of buffer solution

In order to stabilize the pH value of complex mixture the buffer solution was used. A buffer solution was prepared (Walpole buffer solution) and the suitable volume was studied by adding various quantities of buffer solutions. Table (1) indicated that 1.5 ml from buffer solution at pH 5-5.5 could maintain the proper pH value and gave the maximum absorbance at 568 nm.

Effect of dye concentration

The effect of different concentrations of xylenol orange dye (0.1-1.5 ml) from 10^{-3} M

and (0.25 – 2) ml from 10^{-4} M on the absorbance of the resulting complex has been studied. The results in Table (2) showed that 0.5 ml from 10^{-3} M of dye solution gave the best absorbance value at 568 nm.

Effect of surfactant

A double benefit on studying the effect of surfactant cetyltrimethyl ammonium bromide on the complex formation; first it increases the absorbance of the complex thus raising molar absorptivity (ϵ) value and in accordance lowering the detection limit for complex determination and hence increasing the sensitivity of the method for determination. To study its influence, different volumes from 10^{-3} M surfactant were added and the results

gathered in Table (3) showed that it has raised the absorbance slightly by the addition of surfactant, so it has no significant effect on complex formation.

Effect of duration time on stability of the complex

The effect of time on the formation and stability of the complex were studied by measuring the absorbance of Y-xyleneol complex under the optimum studied conditions. It was found that from Table (4) the complex was stable for 1 hour after which the complex began to dissociate.

Stoichiometric ratio of yttrium-xyleneol orange complex

The stoichiometric ratio of Y-xyleneol orange complex was studied and estimated

using the continuous variation method where in this method the molarities of both components (10^{-3} M of Y and xyleneol orange) were varied while the total volume was kept constant to investigate the metal to dye ratio (Y : ligand). Figure (3) showed that from the obtained results the molar ratio of complex was 1:1.

Calibration curve

In order to investigate the effective working range of yttrium concentrations ($\mu\text{g ml}^{-1}$) in which the colored complex adheres to Beer's law, the absorbance of yttrium-xyleneol orange complex was measured against the proper blank at the studied conditions at λ_{max} 568 nm then the absorbance was plotted against a series of different concentrations of yttrium. Figure (4) showed that the calibration curve

Table (1): Effect of buffer solution

Volume taken (ml)	pH 4.5		pH 5		pH 5.5	
	λ	Abs.	λ	Abs.	λ	Abs.
0.5	569.5	0.262	569.5	0.52	568.5	0.55
1	569.5	0.6	569	0.61	568	0.68
1.5	569	0.63	568	0.71	568	0.71
2	569	0.64	568	0.71	568	0.71

Table (2): Effect of dye concentration

Volume from 10^{-3} M (ml)	Absorbance	Volume (ml) from 10^{-4} M	Absorbance
0.1	0.167	0.1	0.015
0.25	0.404	0.25	0.0264
0.4	0.629	0.5	0.05
0.5	0.71	1	0.131
0.7	0.71	1.5	0.207
1	0.71	2	0.213

Table (3): Effect of Surfactant

Volume (ml)	Absorbance
0.1	0.14
0.25	0.33
0.5	0.358
1	0.78
2	0.78

Table (4): Effect of time on the stability of complex

Time (minute)	Absorbance
0	0.71
5	0.71
15	0.71
30	0.71
40	0.71
50	0.71
60	0.71
75	0.65
90	0.63

was linear over the range from 0.2 $\mu\text{g ml}^{-1}$ to 6 $\mu\text{g ml}^{-1}$ with molar absorptivity ϵ value $3.2 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$ and a 0.9978 correlation coefficient value (R^2) 0.9978.

Beer's law, molar absorptivity, Sandell's sensitivity indicated that the method is sensitive, where linearity and the relative standard deviation accuracy for the analysis of five replicate measurements indicated that the method is precise and accurate, as shown in Table (5).

Table (5) characteristics and statistical data for the proposed method

Parameter	Value
Beer's law limit (ppm)	0.2-6
Molar absorptivity ($\text{L mol}^{-1}\text{cm}^{-1}$)	3.2×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	2.7×10^{-3}
Determination coefficient	0.9978
% RSD	1.64%
% error	1.5%
pH	5-5.5
Metal: ligand ratio	1:1
λ_{max} (nm)	568

Effect of interfering anions

The effect of different anion concentrations; Cl^- , NO_3^- , SO_4^{2-} , ClO_4^- on the formation of yttrium-xylenol orange complex were studied under the optimized conditions. From the obtained data in Table (6), it was indicated that the determination of Y in presence of these acidic media was possible up to $0.4 \times 10^{-2} \text{ M}$ for H_2SO_4 , $0.8 \times 10^{-2} \text{ M}$ for HClO_4 , $1.5 \times 10^{-2} \text{ M}$ for HNO_3 and $1.5 \times 10^{-2} \text{ M}$ for HCl without any interference effect.

The effect of accompanying interfering REE elements

The effect of the concomitant interfering rare earth elements in the rare earth concentrate on yttrium determination using xylenol orange complex was studied. A series of concentrations of different elements with a constant concentration of yttrium ($3 \mu\text{g ml}^{-1}$) were prepared and measured against a proper blank at 568 nm. The interference concentration on yttrium was shown in Table (7) which indicated that determination of

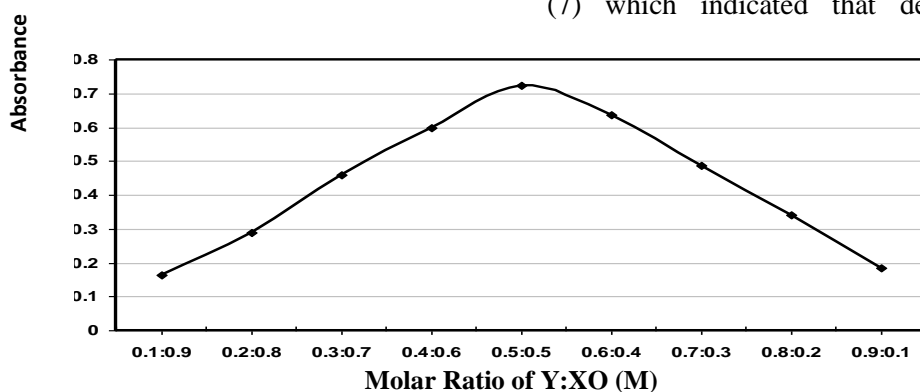


Figure (3): Molar ratio of yttrium to xylenol orange dye

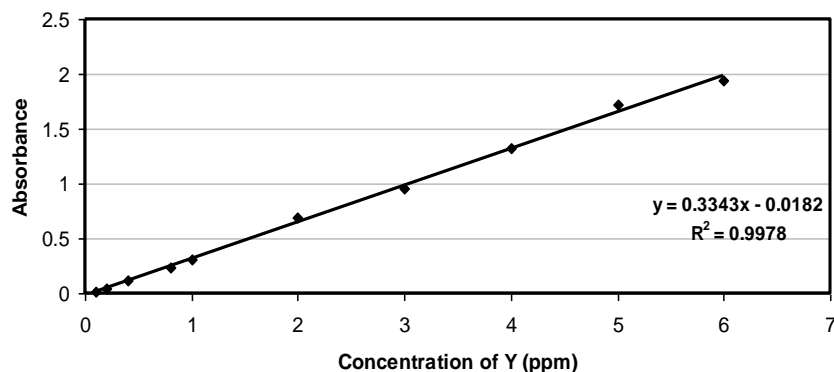


Figure (4): Calibration curve of Yttrium xylenol orange complex

yttrium will be possible below these concentration values and above which causes interference on yttrium determination using the conventional spectrophotometric determination. One of the solutions that may overcome the interference effect was the use of derivative spectrophotometric technique. The first to fourth derivative spectra were investigated. It was found that the first derivative overcome the

interference effect and hence increases the sensitivity, Figure (5). The results showed the performance of linear calibration curve using the first derivative technique from minimum detection limit of 0.2 ppm till a maximum of 5.2 ppm, Figure (6).

From the result of molar absorptivity (ϵ) of the present studied method compared to the previous work done using other chromogenic

Table (6) Effect of interfering anions

Volume (ml)	HClO ₄ (10 ⁻² M)	HNO ₃ (10 ⁻² M)	HCl (10 ⁻² M)	H ₂ SO ₄ (10 ⁻² M)
	Absorbance			
0.2	0.708	0.708	0.70	0.70
0.4	0.708	0.71	0.71	0.70
0.6	0.708	0.71	0.70	0.64
0.8	0.708	0.71	0.70	0.62
1.5	0.66	0.71	0.70	0.59
2	0.61	0.62	0.63	0.58

Table (7): The maximum permissible concentration limits of REE s

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Tm	Yb	Tb	Lu
Conc.(ppm)	0.2	0.2	0.3	0.3	0.2	0.8	2	2	0.8	0.8	1	0.8

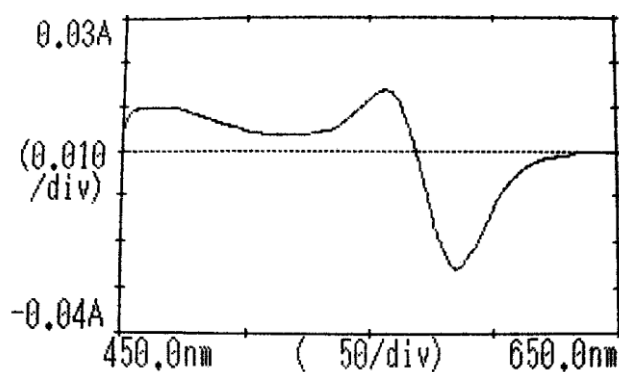


Figure (5): First derivative of standard yttrium (3 µg ml⁻¹)

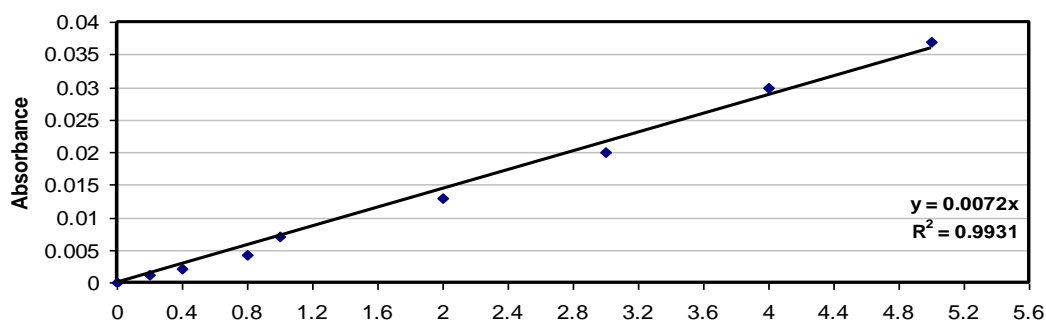


Figure (6): Calibration curve of Yttrium xylenol orange complex using 1st derivative

dyes for yttrium determination shown in Table (8), it can be concluded that the present method is favorably with other methods.

APPLICATION

Two synthetic samples were prepared, the first, *synthetic (1)*, was simulating the composition of rare earth monazite concentrate without Ce, which causes interfering effect either with conventional spectrophotometry or using the first derivative. The second, *synthetic (2)*, constitutes only heavy rare earth elements with yttrium. Another two REE concentrate samples, *sample (1)*, was prepared from monazite and *sample (2)* was prepared from xenotime. Both samples were measured using the advanced instrumental tool, inductively

coupled plasma –optical emission spectroscopy (ICP-OES), and the data were gathered in Table (9). Both the conventional and first derivative methods for determination were applied on all samples and the results were represented in Table (10). The latter illustrated that, the separation of light rare earth elements give results more accurate for yttrium than in total REE (light and heavy ones)⁽²⁷⁾. It can be concluded that Y can be determined accurately in monazite after separation of light REE using conventional or first derivative method. On the other hand, yttrium in xenotime can only be determined by first derivative technique in heavy rare earth concentrate (due to the higher concentrations of heavy REE, as shown in Table (10).

Table (8): Comparative study of spectrophotometric results of yttrium using other chelating organic reagents with the present studied dye

Dye	ϵ ($L\ mol^{-1}\ cm^{-1}$)	L	Beer's law	pH	R.S.D%
Alizarin red S ⁽¹⁾	0.53×10^4	519	1-26	4.9	$\pm 2.33\%$
2,7-diiodoquinoline-8-ol rohadamin6G ⁽¹²⁾	5.3×10^5	540	0-20	-	-
Amino-4-hydroxyanthhrquion ⁽¹⁷⁾	0.9×10^4	580	-	6.2	$\pm 0.5\%$
1-(5-methyl-2-pyridazol)azo-2-naphthol ⁽²⁶⁾	6.4×10^4	530	Upto 1 ppm	9.5-11.5	-
Xylenol orange	3.2×10^4	568	0.2-11.5	5	1.64

Table (9): chemical analysis of the samples analysis (ppm)

Element	La	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	Yb	Tb	Lu	Y
Synthetic(1)	400	50	250	25	15	13	10	3	3	3	1	2	1	50
Synthetic(2)	0	0	0	0	0	0	0	3	3	3	1	2	1	50
Sample 1	397840	44430	268528	35885	19877	17890	10564	227	500	0	100	0	0	65343
Sample 2	400	600	710	1500	50	31520	19644	19440	55100	16166	31750	1190	1500	276540

Table (10): Chemical and statistical analysis of Y for the present studied method

Sample	Concentration present (ppm)	Concentration measured (ppm) Derivative	S.D	% RSD	%E
Synthetic 1	50	76	29.5	38	17.20
Synthetic 2	50	52.6	1.56	3.04	1.36
Sample 1	65343	63423	0.21	3.4	1.54
Sample	276540	267430	1.25	4.6	2.0

CONCLUSIONS

The proposed method involves direct and first derivative spectrophotometric method for determination of yttrium in concentrate REE. It was successfully used with good accuracy after separation of light rare earth elements. In monazite yttrium can be measured using conventional and derivative method but in case of rare earth concentrate from xenotime mineral it was measured using derivative spectrophotometric method due to the presence of high concentrations of heavy rare earth elements.

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التقدير الطيفي اللوني المباشر و المشتق لليتريوم فى ركازات مختلفة من العناصر الأرضية النادرة

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فى هذا العمل تم دراسة تقدير مباشرة ومشتقة طيفية لونية سهلة و دقيقة بإستخدام صبغة الزايلينول البرتقالية (xylene orange) لتقدير الليتريوم فى ركازات العناصر الأرضية النادرة المحضرة من المونازايت و الزينوتيم المصريين. و قد وجد أن منحنى المعايرة (طبقا لقانون بيير) كان خطا مستقيما فى المدى من 0.2 إلى 610 ميكرو جرام لكل مللى عند أفضل طول موجى قيمته 568 نانو متر. لقد تم دراسة عدة عوامل مؤثرة لتكوين أفضل مركب و قد تبين أن أفضل تكوين للمركب كان عند قيمة أس هيدروجينى من 5 إلى 5.5 و تركيز الصبغة 0.5 مللى من 0.003 عيارى و ذلك عند أفضل طول موجى 568 نانومتر. و بعد ضبط هذه العوامل وجد أن قانون بيير كان متوافقا فى النطاق من 0.2 إلى 6 ميكرو جرام لكل مللى و قيمة إمتصاص عيارى (E) 32.0×10^4 لتر لكل مول لكل سم و نسبة مئوية من الإنحراف المعيارى (%RSD) مقدارها 1.64% و نسبة خطأ قيمته 1.50%.