# Spectrophotometric Determination of Lanthanum (III) With Bromopyrogallol Red And Cetylpridinium Chloride - Applications in Natural Waters and Urine

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## Abstract

A highly sensitive spectrophotometric procedure for the estimation of lanthanum in aqueous medium has been established. The method was involved the reaction of lanthanum with bromopyrogallol as chelating agent in the presence of cetylpyridinium chloride at pH4.61 to produce a soluble blue colour ternary complex exhibited maximum absorption at 661nm. The method adheres to Beer's low over the concentration range 0.125 –5.0 µg/ml with coefficient determination (r2= 0.9987). The molar absorptivity(Ɛ) of the ternary complex (La(III)-BPR-CPC) is 5.39x104 M-1cm-1 which corresponds to Sandell's sensitivity index of 0.00258 µg.cm-2. The stoichiometric composition of the ternary complex was estimated and found to be (1:2:4) (La:BPR:CPC), respectively. The values of detection limit (DL) and quantitation limit (QL) were calculated and found to be 0.0630 and 0.0817 µg.ml-1, respectively. A recovery% was found in the range 95.3% to 103.5%, while the precision (RSD) was estimated in the range 0.126 to 1.705. The proposed procedure has been applied successfully for the determination of lanthanum in natural waters and urine sample.

**Keywords:** Lanthanum; Bromopyrogallol red; Surfactant (CPC); Spectrophotometry.

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## INTRODUCTION

Lanthanum (La) is an important element of rare earth group. La is a silvery-white metallic element . It is present in nature together with Ce in the monazite sands and minerals [1]. La is used as additives in glass , carbon arc lamps for studio lights , torches and projectors. It is useful in the manufacturing of expensive lenses for telescope and camera as it imparts high refractive index to the glass. It was added in the manufacturing of steel to improve its properties like ductility and malleability [2] . High purity La is used as catalyst in nuclear and in automobile industries [3]. An excessive amount of La in soil acted as pollutants .It can cause biological concentration , environmental enrichment, and accumulation in the liver [4]. Several analytical methods have been reported for the determination of La.

These methods involve: capillary electrophoresis coupled with UV-Vis detection [5], inductively coupled plasma-optical emission spectroscopy (ICP-OES) [6], inductively coupled plasma- mass spectroscopy (ICP-MS) [7], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [8], potentiometry [9], cloud point extraction(CPE) [10] differential pulse polarography [11]and new design optical sensor [12]. However, most of these analytical methods require elaborate , sophisticated and expensive instruments which may or may not be available in every laboratory , or involve difficult methods of fabrication.

Few of an organic reagents have been employed for the estimation of La by spectrophotometric methods. These reagents include: 2- [(4-Benzyloxy phenyl)azo]-5-nitro-4-phenyl imidazol (BANI) which forms ion association complex with La ion [13] , xylenol orange with cetylpyridinium chloride (CPC) using flow injection analysis [14], o-methoxy phenylthiourea [15], (2-pyridylazo)-2-naphthol (PAN) [16], tribromoarsenazo [17], 2,2′-dipyridyl-2-pyridylhydrazone [18], fast violate blue [19] and methylthymol blue reagent [20]. A Higher order derivative spectrophotometry was also reported recently for the simultaneous determination of La(III) and europium.

This research describes the optimum conditions for development of a sensitive spectrophotometric method to determine La by forming a quaternary complex with an available reagent promopyrogallol red (BPR) reagent and cationic surfactant (CPC) in aqueous solution and to explore its applicability in urine and a number of water samples.

## Experimental

### 2.1.Apparatus

A Jasco V-630 UV-Vis spectrophotometer (Japan) with 1.0-cm matched quartz cells and Bp3001 professional bench top pH meter devices were employed for all absorption spectra recording and pH measurements, respectively.

### 2.2.Reagents

High pure chemical substances were used in all experiments .

- La(III) stock solution (1000µg/ml). A 0.31186 g of La(NO3).6H2O (Fluka) was dissolved in 100 ml distilled water (DW) using a calibrated flask.

- La(III) working solution (100 µg/ml). A 10 ml of the La(III) stock solution was diluted to 100 ml with DW.

- BPR solution (1x10-3M). A 0.13955 g of the reagent of BPR (Fluka) was dissolved in 250 ml DW using a calibrated flask and kept in dark bottle.

-Buffer solution of pH 4.61. This solution was set by mixing 25.5 and 24.5 ml of acetic acid (0.2M) and sodium acetate (0.2M), respectively. The solution was pipetted into a 100 ml calibrated flask and diluted to the mark with DW [21].

-CPC solution (0.1% w/v). A 0.1 g of CPC (Koch-Light) was dissolved in 100 ml DW.

-Tween 20 solution (1% v/v). It was made by diluting 1 ml of tween 20 solution to 100 ml with DW using a calibrated flask.

-Composite mixture solution (1x10-2 M). A 0.1761g of ascorbic acid (BDH) , and 0.2182 g of 5-sulphosalcylic acid (Fluka) were weighed and dissolved in about 80 ml DW. The pH of the resulting mixture was adjusted to 4.61 with NaOH solution (0.1M) . The solution was then transferred to 100 ml calibrated flask and finalised to the mark with the similar solvent. This solution was freshly prepared.

### General procedure

A suitable aliquot containing 2.5 – 100 µg of working La(III) solution(100 µg/ml) was pipetted into 20 ml calibrated flask and mixed with 0.5ml of composite mixture solution (1x10-2 M), 2ml of buffer solution pH 4.61, 2.5ml of BPR reagent (1×10-3M), 3 ml of CPC solution (0.1%) and 2 ml of tween 20 solution(1%). After shaking the mixture of solution thoroughly, the mixture was then left for 10 minutes and made up to the mark with distilled water. The solution was mixed well and record its absorbance at 661 nm against a solution prepared in the same manner but without La(III)(blank).

### Procedure for the determination of la(III) in water samples

After clarifying the sample solution, a suitable volume of the sample solution not extra than 5 ml were taken and the above general procedure designated was followed.

### Procedure for the determination of la(III) in urine

The sample of urine solution was prepared as the procedure described in reference [22] and the pH of the resulting urine solution was then adjusted to 4.61 with 1M NaOH solution. A suitable aliquot of this solution was pipetted out into a 20ml calibrated flask and the La content was then analysed as the general procedure described .

## Result and Discussion

When a 2ml of 1×10-3M BPR reagent solution was pipetted into 20ml of calibrated flask containing 2ml of La working solution and dilute alkaline solution of NaOH, a weak violet binary chelate [La(III)-BPR] was observed and showed maximum absorption at 674 nm versus the corresponding blank solution. But on the addition of a few drops of cationic surfactant solution a sharp increase in colour intensity was observed . This observation led us to the development of a sensitive method for the analysis of La in an aqueous medium . The influence of several parameters on the absorption intensity of the coloured complex was investigated and the conditions of the reaction have been optimized.

### pH effect

The influence of pH on the colour intensity of the complex [La(III)-BPR] was investigated. The results in Fig.1 show that the optimum pH range for the complex formation is 4.61-4.82 and the pH value of 4.61 was designated for the subsequent measurements due to its high sensitivity.

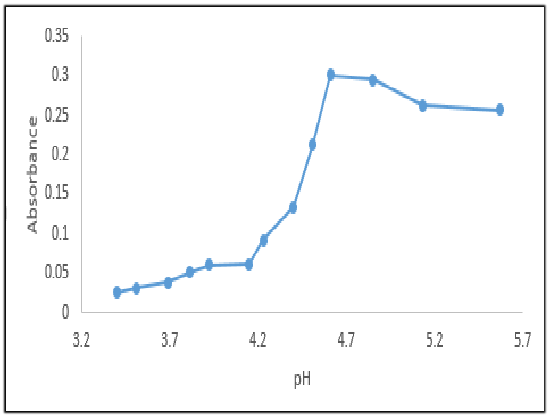

Fig. 1: Effect of pH on absorbance of [La(III)-BPR] complex

### Effect of surfactant

The influence of different amounts 1.0-4.0 ml of various surfactants (CPC, CTAB, SDS , triton-x100 and tween 20) on the absorbance of the resulting [La(III)-BPR] has been investigated. The experimental results illustrated that 3 ml of CPC solution caused high increase in the colour intensity of the complex while no effect was observed in the presence of other surfactants. Therefore, a 3ml of it have been chosen for the subsequent experiments.

### Effect of CPC and tween 20 solutions

The presence of tween 20 in the reaction mixture was necessary in removing the slight turbidity that is may be formed in the solution. The effect of tween 20 and CPC solutions were examined for this purpose .The results are listed in Table 1 show that a 2 ml of tween 20 and 3 ml of CPC solutions have been used for subsequent experiments for the following reasons : (i) the reaction of La with BPR reagent was accelerated, (ii) turbidity of the solution was disappeared [17] , (iii) the colour contrast of the La (III)-BPR reaction was more improved and caused increasing in the sensitivity . Triton x-100 and CPC have been also tried but the results obtained were not as useful as those with tween 20 .

### Effect of reagent amount

The influence of different amounts of BPR reagent in the presence of CPC with respect to La on the colour intensity of the ternary complex (La(III)-BPR-CPC) was investigated. The experimental results indicated that a 2.5 ml of 1x10-3M BPR reagent can be considered optimum because of its highest colour sensitivity and lowest corresponding blank value.

Table 1: Effect of surfactants on absorbance

| **ml of tween 20 solution (1%)** | **ml of CPC solution (0.1%)** | **Absorbance** | | **λ max (nm)** |
|---|---|---|---|---|
| | | **sample** | **Blank** | |
| 1.0 | 2.0 | 0.7065 | 0.0634 | 664 |
| 1.0 | 2.5 | 0.7183 | 0.0652 | 661 |
| 1.0 | 3.0 | 0.7332 | 0.0578 | 661 |
| 1.0 | 4.0 | turbid | - | 655 |
| 1.5 | 2.0 | 0.7944 | 0.0672 | 664 |
| 1.5 | 2.5 | 0.7901 | 0.0732 | 660 |
| 1.5 | 3.0 | 0.8012 | 0.0745 | 659 |
| 1.5 | 4.0 | turbid | 0.0820 | 653 |
| 2.0 | 2.0 | 0.8140 | 0.0605 | 664 |
| 2.0 | 2.5 | 0.8131 | 0.0718 | 661 |
| 2.0 | 3.0 | 0.8230 | 0.0523 | 661 |
| 2.0 | 4.0 | 0.7902 | 0.0855 | 654 |
| 3.0 | 2.0 | 0.7882 | 0.0823 | 655 |
| 3.0 | 2.5 | 0.7871 | 0.0673 | 657 |
| 3.0 | 3.0 | 0.7711 | 0.0707 | 655 |
| 3.0 | 4.0 | 0.7701 | 0.0791 | 656 |

### Effect of temperature and reaction time

For the purpose of studying the influence of temperature and time on the formation La-BPR complex and its stability, the reaction was carried out at different temperatures using a water bath with different periods of time. Table 2 shows the results achieved.

Table 2: The influence of temperature and time on the absorbance of complex

| Temperature (C°) | Absorbance/minute | | | | |
|---|---|---|---|---|---|
| | 1.0 | 5.0 | 10 | 15 | 20 |
| 5.0 | 0.6931 | 0.6741 | 0.6548 | 0.6345 | 0.6007 |
| RT* | 0.8291 | 0.8381 | 0.8433 | 0.8436 | 0.8447 |
| 30 | 0.8511 | 0.8912 | 0.9291 | 0.9451 | 0.9622 |
| 50 | 0.8854 | 0.9327 | 0.9412 | 0.9666 | 0.9713 |

*RT= Room Temperature = 20 ± 2 C °

The results in Table 2 show that when the reaction was conducted at temperatures 30 and 50 C°, a noticeable rise and instability in the absorbance readings of the complex formed were observed with increasing time. While the reaction at low temperatures 5Cº, cause decrease in the colour intensity of complex in comparison with the results obtained at laboratory temperature. the results showed a remarkable improvement after a waiting time of 10 minutes from the reaction time, so the laboratory temperature was adopted with a waiting time of 10 minutes in subsequent experiments .

### Effect of Masking agent

The effect of different amounts of various masking agents on absorption of the ternary complex was investigated. The results are shown in Table 3.

Table 3: Effect of masking agent on absorbance of 2.5 µg/ml La(III) ion

| Masking agent (0.01M)* | Absorbance/ml of masking agent added | | |
|---|---|---|---|
| | 0.5 | 1.0 | 2.0 |
| EDTA | 0.0038 | 0.0015 | 0.0011 |
| NaF | 0.0059 | 0.0035 | 0.0012 |
| Ascorbic acid | 0.8391 | 0.8212 | 0.8288 |
| 5-sulfosalicylic acid | 0.8431 | 0.8411 | 0.8221 |
| Tartaric acid | 0.5344 | 0.5182 | 0.3113 |

*The pH of masking solutions were adjusted to 4.61 ,

Absorbance without masking agents=0.8433

The results in Table 3 indicate that ascorbic acid , 5-sulfosalicylic acid solutions have no effect on the absorbance of [La(III)-BPR-CPC] complex, while other masking agents (EDTA and NaF) cause decreasing in the sensitivity may be owing to their complexing action with La(III) ion.

Therefore, a composite mixture solution of (5-sulfosalicylic acid and ascorbic acid) was prepared and its effect on the absorbance of coloured complex was then studied. The investigational results reveal that 0.5 ml of the composite mixture solution was optimum and therefore, it was selected for the subsequent experiments.

Reproducibility and Validity of Beer's law

Under the optimal operating conditions, a linear calibration graph was obtained in the concentration range 0.125- 5.0 µg.ml-1 of La ion and determination coefficient (r2=0.9987 )(Fig.2). The apparent molar absorptivity(Ɛ) of the ternary complex La-BPR-CPC and the index of Sandell's sensitivity were found to be 5.39x104 l.mol-1cm-1 and 0.00258 µg.cm-2, respectively. The detection limit (DL) and quantification limit (QL) were estimated and equal to 0.0630 and 0.0817 µg.ml-1, respectively.

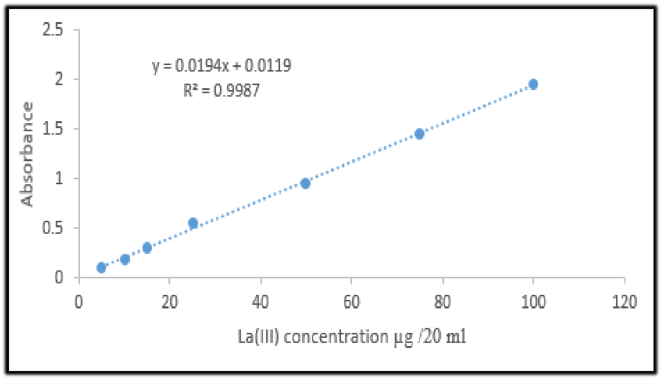

Fig. 2: Calibration graph for La) III) determination according the recommended procedure

Final absorption spectra

According to the optimum conditions of proposed procedure, La ion forms a purple-blue water soluble ternary complex (La(III)-BPR-CPC ) at pH 4.61. The coloured complex exhibits one maximum absorption band located at 661 nm against the blank solution which was prepared in the identical manner but without La (Fig. 3).

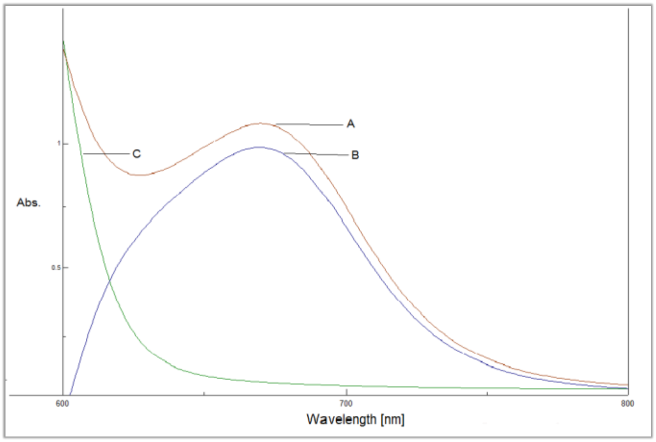

Fig. 3: The absorption spectra of 2.5 ppm of La(III) (A) sample against DW and (B) sample against blank solution (C) Blank against DW

### Stoichiometry of the resulting complex

The Composition of the reaction of La(III) and BPR to form the complex was carried out under the established conditions by applying the continuous variations (Job) and mole ratio methods [23]. In Fig.4 , the results of both methods reveal that the ratio of La(III) : BPR in the complex was found to be 1:2. The mole ratio method was also applied for estimating the ratio of CPC to the complex (La(III):BPR) and the results in Fig.5 indicate that the ratio of La(III):BPR:CPC was found to be 1:2:4, respectively. The stability constant of the complex was also calculated (Ks= 7.58x109 M-2 ) [24].

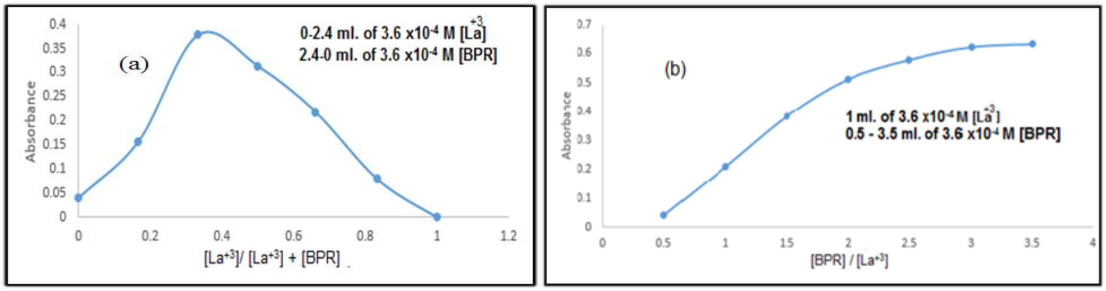

Fig. 4: (a) Continuous variations(Job) and (b) mole-ratio plots for La(III) – BPR complex.

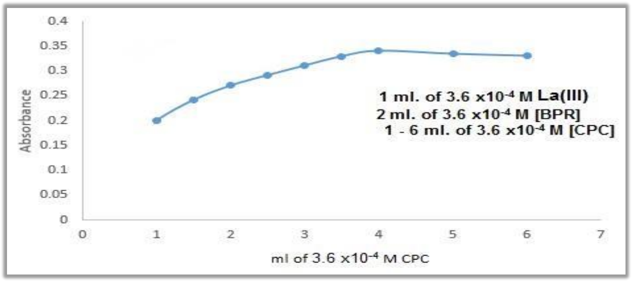

Fig. 5: Mole-ratio plot for La(III)-BPR-CPC complex.

## Effect of foreign ions

In order to assess the possible analytical applications of the recommended procedure. The influence of different amounts 10, 25, 50, 100, 250, 500 µg of a number of foreign ions on the absorbance of (La(III)-BPR-CPC) complex at pH4.6 was investigated. An error of ±5% in absorbance is considered tolerable. The results are listed in (Table 4).

Table 4: The tolerance limit of Individual extraneous ions on the determination of 25 µg of La ion.

| **Foreign ion** | **Tolerance limit (µg)** |
|---|---|
| $Na^+$, $Cl^-$ , $Br^-$ , $NO_3^-$ , $CO_3^{2-}$ , $Pb^{2+}$ , $Be^{2+}$, ascorbic acid | 500 |
| $Ca^{2+}$ , $K^+$, $SO_4^{2-}$ ,$HCO_3^-$ | 250 |
| $Zr^{4+}$, $IO_3^-$, $Co^{2+}$, $Ba^{2+}$, $Se^{4+}$ ,$CH_3COO^-$ | 100 |
| $Mg^{+2}$ | 50 |
| $PO_4^{3-}$, $Ni^{2+}$, $Fe^{2+}$ | 25 |
| $Te^{4+}$, $Fe^{3+}$, $Mn^{2+}$, $Pd^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cr^{6+}$, $Bi^{3+}$ | ≤10 |

As shown in Table 4. The largest interferences were found for Te4+, Fe3+, Mn2+, Pd2+, Cu2+, Cd2+, Bi3+and Cr6+ ions .

## Application

The recommended procedure has been successfully applied for the estimation of La at two different concentrations 25 and 50 µg added to a volume not more than 5ml of natural waters ( tap, river , mineral ,well and Shatt Al Arab waters) and urine sample. The results are collected in (Table 5) and reveal that the suggested procedure is suitable for estimating La(III) with agreeable results.

Table 5 : Estimation of La in natural waters and urine sample

| Type of sample | Sample (ml) | Recovery(%)±RSD*/µg of La added | |
|---|---|---|---|
| | | 25 | 50 |
| River water<br>(Tigris river-Mosul) | 2 | 96.03±0.163 | 98.18±0.289 |
| | 5 | 95.7±0.732 | 100.3±1.508 |
| Well water[(a)] | 2 | 95.89±1.099 | 99.9±0.549 |
| | 5 | 95.3±1.013 | 102.7±0.740 |
| Tap water | 2 | 97.60±0.921 | 96.75±0.157 |
| | 5 | 96.3±0.214 | 103.5±0.218 |
| Mineral water[(b)] | 2 | 98.2±0.296 | 101.1±0.223 |
| | 5 | 99.4±0.175 | 103.5±0.126 |
| Shatt Al Arab water [(c)]<br>(Basrah - Iraq) | 2 | 100.2±1.705 | 101.6±0.499 |
| | 5 | 101.9±0.376 | 102.7±0.350 |
| Urine | 1 | 97.2±0.475 | 99.7±0.601 |
| | 2 | 95.3±0.504 | 96.4±0.451 |

*Average of three estimations ,

(a) from Sadda and Ba'wiza area in Mousl city

(b) Mineral water manufactured by (life) company

(c) Water of Shatt Al Arab,

For estimating the efficiency of the proposed procedure , a t-value test was carried out for three different samples and the results are summarized in Table 6.

Table 6 : Determination of 50 µg La(III) in natural waters and urine sample

| Type of sample | ml of Sample | La(III) found* (µg) | (Recovery%±RSD)* | t-exp.# |
|---|---|---|---|---|
| Shatt Al Arab water | 5.0 | 50.50 | 101.00±0.436 | 1.50 |
| Urine | 1.0 | 48.54 | 97.08±0.359 | 1.93 |
| River water | 2.0 | 50.38 | 100.76±0.175 | 0.77 |

*Average of five estimations , $\# \pm t = (\bar{x} - \mu)\frac{\sqrt{N}}{S}$ ,
Tabulated “t”value at 95% confidence level of 95% is equal to 2.776 for ( N= 4)

The results in Table 6 indicate that the measured t values are less than the tabulated (t) values at the 95% confidence level and for four degrees of freedom [25]. These results reveal that there is no a determinate error in the recommended procedure.

## Conclusion:

In this work La in aqueous medium was estimated by using available chelating agent of bromopyrogallol red (BPR) in the presence of CPC to form ternary soluble complex (La(III)-BPR-CPC) at pH4.61. the suggested method is highly sensitive and suitable for the determination of La in some natural waters and urine sample.

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