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# SPECTROPHOTOMETRIC STUDIES AND ANALYTICAL APPLICATION OF CERIUM ( III ) AND THORIUM ( IV ) CHELATES WITH PYRIDINE -2- ALDEHYDE -2- PYRIDYLHYDRAZONE ( PAPH )

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- ملخـــص -

لقد وجد أن عنصر السيريوم الثلاثي والثوريوم الرباعي يتفاعلان مع المركب العضوي بيريدين -٢- الدهيد -٢- بيريديل هيدرازون في الوسط المائي الذي يحتوي على ٥٠ ٪ كحول ايثلي في محاليل ذات أرقام هيدروجينية تساوي ٧,٧٥ ، ٨,٤٥ على التوالي . كذلك تطبيق قانون بير على هذه التفاعلات لتقدير تراكيز منخفضة من هذه العناصر وان هذه الطريقة تعتبر حساسة جداً إذ ان معامل الامتصاص الجزيئي هو ٢,٥٦ × ١٠ ٤ ، ٣,٧ × ١٠ ٤ لتر مول -١ سم -١ لكل من عنصري السيريوم الثلاثي والثوريوم الرباعي على التوالي . كذلك تم تعيين تركيب وثبات المتراكب الذي يتكون بين تلك العناصر والمركب العضوي . هذا وقد قمنا بدراسة تأثير وجود بعض الايونات على تقدير هذه العناصر .

## ABSTRACT

Ce ( III ) and Th (IV) reacts with pyridine–2–aldehyde–2–pyridylhydrazone in aqueous solutions containing 50 % ethanol at pH's 7.75 and 8.45 respectively. Beer's law is obeyed over the range 0.0–15.$\mu$g and 0.0–18 $\mu$g of cerium and thorium respectively . The proposed procedure is sensitive , since molar absortivity is $2.56 \times 10^4$ and $3.60 \times 10^4$ $l.mol^{-1}$ $cm^{-1}$ for Ce ( III ) and Th (IV) respectively . The composition and stability of these complexes have been determined . The limitation of this procedure and the effect of other ions have been studied .

## INTRODUCTION

Hydrazones, particularly hydrazones of nitrogen – containing heterocyclics have attracted much attention as analytical reagents , because of their high sensitivity and selectivity . Lions et.al[1,2] first reported the analytical properties of these compounds . Their analytical applications have recently been reviewed by Katyal et. al[3] . Various substituted hydrazones have been used for the spectrophotometric determination of several metal ions[4–15] .

Following our studies in search of new analytical reagents for the spectrophotometric determination of Ce ( III ) and Th ( IV )[16–21] , it was found that the pyridine–2–aldehyde–2–Pyridylhydrazone ( PAPH ) undergoes a practically sensitive reaction with the above elements . However nothing has yet been reported about the complexes of PAPH with Ce ( III ) and Th ( IV ) ions .

This paper describes the spectrophotometric studies on composition , stability and analytical application of Ce ( III ) and Th ( IV ) Chelates with PAPH in buffer solutions containing 50% ethanol .

## EXPERIMNTAL

**reagents :**

All solutions were prepared with analytical–reagent grade chemicals in doubly distilled water unless indicated otherwise.

PAPH reagent : PAPH was prepared as previously described by lions[1] . An ethanolic solutions of PAPH ( $10^{-3}$M ) were prepared and stored in an amber–glass bottom . Buffer Solutions : The buffer solutions used were perchloric acid for pH values below 3.5, acetic acid–sodium acetate mixture for pH values between 3.5 –6.0, boric acid – borax mixture for pH values between 6.5–9.0, borax–sodium hydroxide mixture for pH values between 9.5–11.0 , and sodium hudroxide for pH values above 11.0 .

Ce ( III ) and Th ( IV ) Solutions : Solutions of Ce ( III ) and Th ( IV ) were prepared using ANALAR grade nitrate salts .

**Apparatus :**

Absorbance curves were measured with a pye Unicam SP8–100 Spectrophotometer . A corning model 12 pH meter was used for pH measurements .

**procedure :**

To a suitable aliquot containing 40 to 80 $\mu$g of Ce ( III ) or Th ( IV ) , add 7.5ml buffer solution , 7.5ml of alcohol and 5ml of $1.0 \times 10^{-4}$ M PAPH solutions . Dilute to 25ml with distilled water and shake well. Measure the absorbance in a 1–cm cell against a reagent blank after 15 min at 205 nm for Ce ( III )–PAPH and at 200 nm for Th (IV)–PAPH chelates .

## RESULTS AND DISCUSSION

**Absorption Spectra :**

The absorption spectra of the liqand PAPH and of its complexes with Ce ( III ) and Th ( IV ) are shown in Fig. 1. It is evident that the maximum absorption of the Ce ( III ) and Th ( IV ) complexes is at 205 and 200 nm respectively . The PAPH does not absorb at these wavelengths .

**The Effect of pH :**

The formation of PAPH complexes with Ce ( III ) and Th (IV) is highly dependent on pH. Fig. 2 shows the dependence of absorption on pH . From these results it can be concluded that the maximum colour development of the above complexes is achieved by buffering at pH 7.75 and 8.45 for Ce ( III ) and Th (IV) complexes respectively

**composition of the complexes**

The composition of Ce ( III ) and Th (IV) complexes , as determined by both the continuous variation and the mole–ratio methods , was shown to have a metal to ligand ratio of 1:2

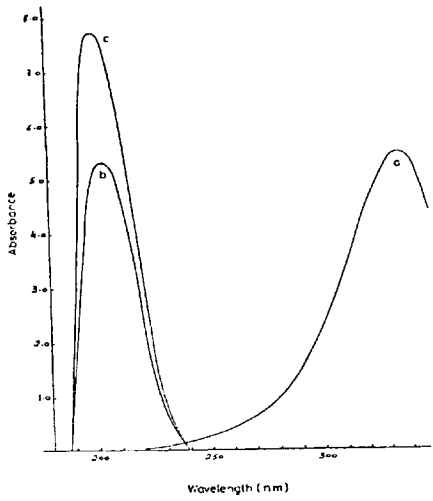


Fig. 1 Absorption spectra of PAPH and its complexes :
(a) PAPH
(b) Ce ( III )–PAPH complex at pH 7.75
(c) Th (IV)–PAPH complex at pH 8.45

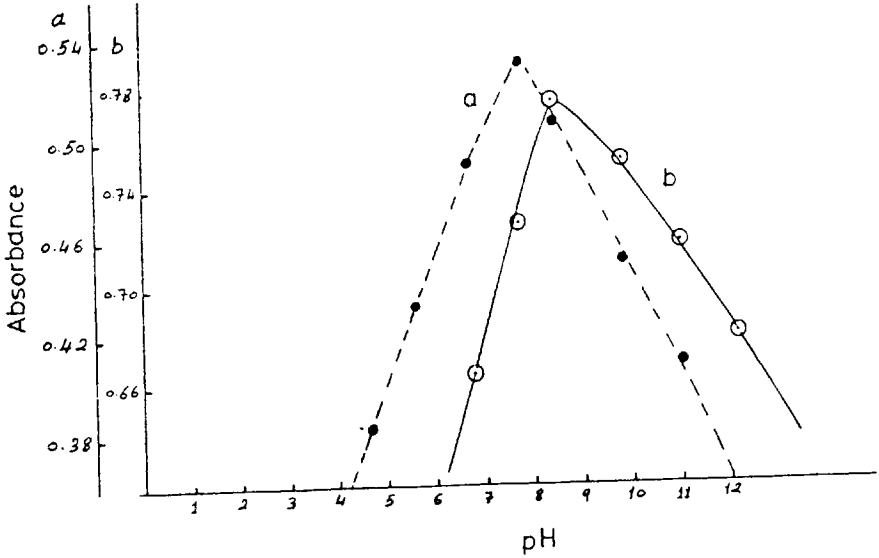


Fig.2 pH dependence of metal complexes :
(a) Ce ( III ) PAPH complex .
(b) Th (IV)–PAPH complex .

**Stability and formation of complexes :**

. The formation of the complexes of Ce ( III ) and Th (IV) with PAPH is instantaneous. However, a 10–min standing period was allowed for equilibration. Measurement of the absorbance was therefore carried out 15 min after the addition of PAPH and the absorbance remained constant for 24 h.

The mean values of the apparent stability constant ( log B ) as well as the values of $-\triangle G^{\circ}$ calculated from the present results are given in Table 1 .

**Table 1 .**

Values of log $\beta$ , $-\triangle G^{\circ}$ and $\varepsilon$ for PAPH complexes .

| Type of Complex | | Log $\beta$ | $-\triangle G^{\circ}$ (KCal/mol) | $\varepsilon$ $l.mol^{-1}cm^{-1}$ |
|---|---|---|---|---|
| Th ( IV ) | : 2 PAPH | 10.30 | 13.99 | $3.70 \times 10^4$ |
| Ce ( III ) | : 2 PAPH | 9.45 | 12.84 | $2.56 \times 10^4$ |

**Beer's Law and Molar Absorptivity :**

Series of standard solutions of Ce ( III ) and Th (IV) were prepared and complexed with PAPH and then the absorbance of each standard solution was measured following the procedure recommended above. Beer's Law is valid in the range 0.0–15 $\mu$g/ml Ce ( III ) and in the rane 0.0–18$\mu$g/ml Th (IV). The molar absorptivities, as calculated from the linear parts of Beer's law plots, were $2.56 \times 10^4$, and $3.70 \times 10^4$ $l\ mol^{-1}\ cm^{-1}$ for Ce ( III ) and Th (IV) respectively ( Table 1 ).

**Comparison With Some Other Reagents :**

Tables 2 and 3 presents a comparison of the most sensitive reagents for the spectrophotometric determination of Ce ( III ) and Th (IV). The use of PAPH as a reagent for Ce ( III ) and Th (IV) compares favourably in respect of sensitivity with these reagents. Hence it is evident that the methods reported[16,18], involving 5–Br–PADAP for the determination of Ce ( III ) and Th (IV) are more sensitive than other methods.

**Effect of Other Ions :**

Synthetic solutions containing a known amount of Ce ( III ) and Th (IV) and various amounts of other ions were prepared and the recommended general procedures for the determination of Ce ( III ) and Th (IV) was followed . The tolerance limit of an ion was fixed as the maximum amount causing an error no greater than 2% in the absorbance of the solution .

There was no interference from the following ions : chlorate, fluoride, nitrate ( 250 $\mu$g) sulphite, sulphate, carbonate, acetate, citrate, tartrate , chloride ( 500$\mu$g) ,

No evidence was found in work previously described[12], to support complex formation in aqueous solutions containing PAPH and the metals Mg ( II ) , Ca ( II ) , Sr ( II ) , Ba ( II ) , Al ( III ) , La ( III ) , Mo ( VI ) , W ( VI ) , Tl ( I ) Sn ( IV ) and As ( III ) . These metals should not interfere and therefore were not tested , Mn(II ) , Fe( II ) ( 100 $\mu$g ) should not interfere also . Smaller amounts of Cu ( II ), Bi ( III ) , Co ( II ) and Ni ( II ) ( $>$ 10$\mu$g)caused interfernce.Oxalate, Bromide and Iodide interfered seriously .

**Table 2.**

Sensitivities of methods for spectrophotometric determination of Ce ( III ) .

| Method | $\epsilon$ ($l\,mol^{-1}cm^{-1}$) | Reference |
|---|---|---|
| – Alizarin Complexone | $3.0 \times 10^3$ | 22 |
| – Arsenazo III | $23.5 \times 10^3$ | 23 |
| – 2– (5–bromo–2–Pyridylazo)–5–Diethylaminophenol | $53.0 \times 10^3$ | 18 |
| –1–(2–Pyridylazo) –2–naphthol | $3.95 \times 10^3$ | 17 |
| – ß -Phenoxyvinyl Phosphoric acid | $3.60 \times 10^3$ | 24 |
| –Pyridine–2–aldehyde–2–Pyridylhydrazone | $25.6 \times 10^3$ | Present |

**Table 3.**

Sensitivities of methods for spectrophotometric determination of Th (IV) .

| Method | $\epsilon$ ($l\,mol^{-1}cm^{-1}$) | Reference |
|---|---|---|
| Acid Alizarin Black SN | $2.3 \times 10^4$ | 25 |
| p–hydroxy,m–methoxybenzylidene 2–aminopyridine | $9.7 \times 10^3$ | 26 |
| Salicylidene–2–aminopyridine | $1.1 \times 10^4$ | 26 |
| p–Hydroxybenzylidene–2–aminopyridine | $1.0 \times 10^3$ | 26 |
| Xylenol orange and Cetyltrimethylammonium bromide | $5.5 \times 10^4$ | 27 |
| 2–(5–bromo–2–pyridylazo)–5–Diethylaminophenol | $1.66 \times 10^5$ | 16 |
| Pyridine–2–aldehyde–2–Pyridylhydrazone | $3.70 \times 10^4$ | Present |

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