

# Spectrophotometric determination of cerium (IV) using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone

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## Summary

A spectrophotometric method was developed for the determination of cerium (IV) based upon the reaction with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP). Cerium (IV) was extracted from aqueous solution of pH 5.5 into chloroform as PMBP complex. The complex exhibits its maximal absorption at around 490nm with the molar absorptivity of  $2.1 \times 10^3 \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ . Formation of a 4 : 1 complex of PMBP with cerium (IV) was confirmed by the molar ratio method. The co-existence of Fe (III) and Cu interfered seriously with determination of cerium (IV). The coefficient of variation for five determinations was 1.1% for 100 $\mu\text{g}$  of cerium (IV). The detection limit for cerium (IV) in chloroform was found to be about 2 $\mu\text{g}/\text{cm}^3$ .

## Introduction

Several spectrophotometric methods based on the use of xylenol orange<sup>1)</sup> O-tolidine<sup>2,3)</sup> and methylene blue<sup>4)</sup> have been reported for the determination of trace cerium. These spectrophotometric methods suffer from various difficulties, including interference from metals commonly associated with cerium.

We now report on 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) as a selective reagent for the spectrophotometric determination of cerium (IV). PMBP is a  $\beta$ -diketone and exists in both keto and enol forms<sup>5)</sup>, which were found to behave similarly in the chemical reactions. A number of studies<sup>6,7)</sup> have been made for the tautomerism of this compound. In the present work, the keto form is used for determination of cerium (IV). In previous paper, we have described<sup>8)</sup> an atomic absorption spectrometric method using PMBP as a chelating agent, and found that it is very useful for the extraction of many cations. We have more recently reported<sup>9)</sup> the HPLC separation of metal pyrazolonates. It appears that PMBP would be an ideal ligand to use for separations of multi-element mixtures by HPLC because of its ability to complex with many metals to produce neutral chelates with high molar absorptivities. Also, PMBP and similar compounds derived from 1-phenyl-3-methyl-5-pyrazolone have been used for the spectrophotometric determination of iron (III)<sup>10)</sup> and vanadium (V)<sup>11)</sup>.

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PMBP reacts with cerium (IV) to give a brown-black complex, which is extracted into chloroform in the pH range 4.9-6.0. This paper describes a selective and simple procedure for the spectrophotometric determination of cerium (IV) with PMBP, as part of an investigation on the use of 4-acyl-5-pyrazolone derivatives as analytical reagents.

### Experimental

A Shimadzu UV-210 double-beam spectrophotometer with a 1-cm silica cell was used for the absorbance measurements. A Toa Denpa HM-5BS pH meter was used for pH measurements.

PMBP : used as 0.01M solution in chloroform. Cerium (IV) standard solution : prepared by dissolving 0.7825g of  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  in  $10\text{cm}^3$  of  $\text{HNO}_3$  and diluting to  $200\text{cm}^3$  with distilled water. Buffer solution : prepared by mixing with an appropriate acetic acid (1M) and sodium acetate solution (1M). All other reagents used were of analytical reagent grade.

The procedure for the synthesis of PMBP is as follows : 1-phenyl-3-methyl-5-pyrazolone (50g) was dissolved in  $300\text{cm}^3$  of dioxane with gentle heating. Calcium hydroxide (42g) was added and  $35\text{cm}^3$  of benzoyl chloride were added dropwise with stirring. The mixture was refluxed for 30min at  $60^\circ\text{C}$  in water bath until the yellow calcium complex was formed. The complex was decomposed by adding  $100\text{cm}^3$  of 3M hydrochloric acid, which caused cream-coloured crystals to separate. The compound obtained was recrystallized from ethanol-water containing a few  $\text{cm}^3$  of diluted hydrochloric acid to destroy any undecomposed calcium complex.

### Procedure

To  $10\text{cm}^3$  of sample solution in a separating funnel containing up to  $300\mu\text{g}$  of cerium (IV), add  $10\text{cm}^3$  of buffer solution (pH5.5) and dilute to  $30\text{cm}^3$  with distilled water. Shake vigorously for 5 min with  $5\text{cm}^3$  of 0.01M PMBP in chloroform. Allow the phases to separate and transfer the organic layer into a silica cell. Measure the absorbance, at 490nm, of the organic layer against the pure chloroform. Beer's law was obeyed up to at least  $800\mu\text{g}$  of cerium (IV) in  $5\text{cm}^3$  of chloroform solution and the molar absorptivity of the complex,  $\epsilon$ , was  $2.1 \times 10^3 \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ .

### Results and discussion

The Ce (IV)-complex exhibits an absorption maximum in the range 480-490nm, while PMBP itself does not show any absorptivity at this wavelength. The optimal wavelength for measurement of the Ce (IV)-PMBP complex is found to be 490nm, against a chloroform.

The effect of pH on the extraction of the cerium (IV) was studied by varying the pH of the aqueous solution from 2.5 to 6.5. As can be seen from Fig. 1, constant absorbance was obtained at narrow pH range of 4.9-6.0, therefore in the extraction

of cerium (IV) the pH of the aqueous solution was adjusted to 5.5 with acetate buffer solution in all subsequent work. The extraction rate for cerium (IV) at pH 5.5 is fast, so shaking for 5 min is sufficient to produce extraction of cerium (IV). The absorbance of the complex in chloroform remains constant for at least 5h. In order to study the effect of the concentration PMBP in chloroform, PMBP was varied from 0.001 to 0.01M for the extraction of  $300\mu\text{g}$  of cerium (IV). It was found that  $5\text{cm}^3$  of 0.01M PMBP solution is sufficient for the quantitative extraction of up to at least  $800\mu\text{g}$  of cerium (IV). For the general procedure, 0.01M PMBP solution is recommended. The calibration curve (Fig.2) for cerium (IV) was linear over the range studied ( $0-800\mu\text{g}/5\text{cm}^3$ ).

In order to learn the details of the formula of the Ce (IV)-PMBP complex extracted in chloroform, we have studied the molar ratio method. The stoichiometry of the complex is shown to be 1 : 4 metal to ligand as can be seen from Fig.3. We further studied the formula of the solid Ce (IV)-PMBP complex which was synthesized by mixing  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  and a methanolic solution of PMBP in 1 : 4 molar ratio at approximately pH 5. The reaction mixture was magnetically stirred in a beaker

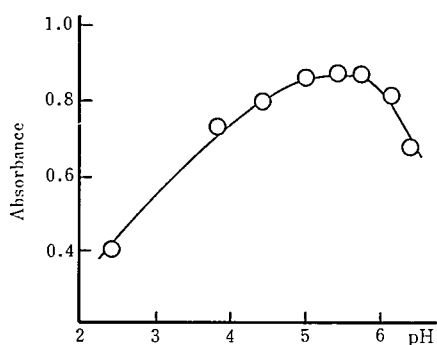


Fig. 1 Effect of pH on the extraction of Ce (IV)  
Ce (IV) :  $300\mu\text{g}$  ; Chloroform :  $5\text{cm}^3$  ; Aqueous phase :  $30\text{cm}^3$

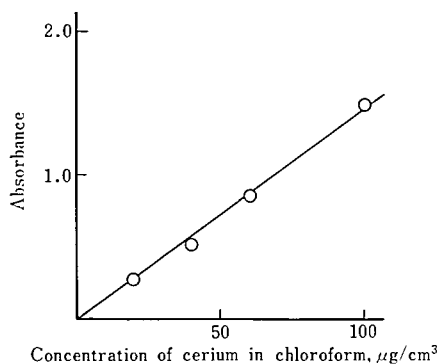


Fig. 2 Calibration curve for Ce (IV)

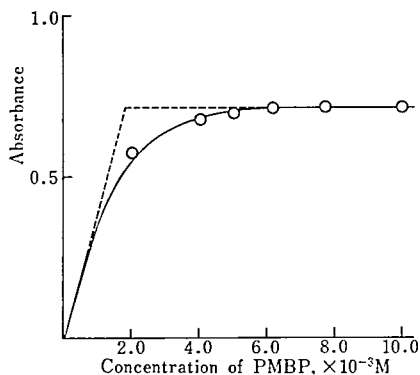
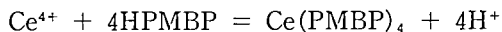


Fig. 3 Effect of concentration of PMBP in chloroform  
 Ce (IV) : 300  $\mu$ g ; Chloroform : 5cm<sup>3</sup> ; Aqueous phase : 30cm<sup>3</sup>

for 1h in a waterbath at 70–80°C. The complex formed was filtered off, washed with water and then methanol several times to remove the unreacted PMBP, and finally dried in vacuo. The complex was analysed by the elemental analysis technique. The analytical data are summarised in Table 1. The results obtained correspond to the theoretical formula, Ce (PMBP)<sub>4</sub>. Thus, the extraction process is represented by the equation



The precision of the method was studied by measuring the absorbance of five solutions, each containing 100  $\mu$ g of cerium (IV), in the absence of other metals. The coefficient of variation was 1.1%. The detection limit for cerium (IV) in chloroform was found to be about 2ppm. Various cations such as Al, Cd, Co, Cu, Fe (III), Mn (II), Ni, Pd, La, Nd and Y were examined individually for their effect on the determination of cerium (IV). For this study different amounts of ionic species were added to the solution containing 300  $\mu$ g of cerium (IV). The results showed that a number of common metal ions tested did not interfere at the 1mg level with determination of cerium (IV). When 1mg of Cu was present, remarkable interferences were found. Also the presence of the Fe (III) below 10  $\mu$ g interfered with determination of cerium (IV). Copper and Fe (III) react with PMBP and their complexes exhibit absorption maxima at around 490nm, indicating the positive error in the absorbance measurement. Thus when large amounts of these metal ions coexist with cerium (IV),

Table 1 Elemental analysis of Ce-PMBP complex

Elements	Found (%)	Calculated (%)
C	65.61	65.37
N	8.97	8.97
H	4.18	4.19

it is necessary to separate or to mask them before using the proposed method. Aluminium and rare earth metal ions react firmly with PMBP to give colorless at pH 5.5, and hence the amount of the complexing agent became insufficient to extract the cerium (IV) for high their concentration, but this effect can easily be overcome by the addition of a sufficient excess of PMBP. In the case of cerium (III), the ion was extracted by PMBP-chloroform solution as a colorless complex under the same conditions with cerium (IV). However, the colour of the extractant was developed to the absorbance increased gradually with passage of time. We consider that the observed colour change of the above complex is due to the varying of Ce (III)-PMBP into the Ce (IV)-PMBP. At adequate pH values PMBP forms colored complexes with only a few metal ions, thereby it imparts considerable selectivity in the spectrophotometric determination of these ions.

Selective and sensitive methods for the spectrophotometric determination of cerium are of great importance because the metal generally occurs in its sources along with other rare earth elements which interfere with the determination of cerium. Though cerium (IV) can be determined sensitively with xylenol orange<sup>11)</sup> or by the fluorometric method<sup>12)</sup>, the advantage of PMBP lies in its selectivity and the simplicity of the procedure.

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