INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF CERIC ION IN AQUEOUS SOLUTION[+]

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Abstract

A new simple and rapid colorimetric method for the determination of ceric ion is described. It is based on the effect of ceric ion as oxidizing agent in the coupling of phenothiazine and sulphacetamide sodium to give an intense bluish-green water-soluble dye with maximum absorption at 614 nm. A graph of absorbance versus concentration shows that Beer's law is obeyed over the concentration range 7-840 µg of ceric ion in a final volume of 25 ml (i.e., 0.28-33.6 ppm), with a molar absorptivity of 4.52×10^3 $l.mol^{-1}.cm^{-1}$, and Sandell sensitivity of 0.0310 $\mu g.cm^{-2}$,with a relative error of less than ± 2.8% and a relative standard deviation of better than ± 3% depending on the concentration.

Keywords: Ceric ion determination, phenothiazine, sulphacetamide sodium, spectrophotometry.

المستخلص

يتضمن هذا البحث طريقة لونية جديدة وبسيطة وسريعة لتقدير ايون السيريك . تعتمد الطريقة على تفاعل ايون السيريك كعامل مؤكسد في تفاعل الفينوثايازين والسلفا اسيتاميد لتكوين صبغة خضراء-مزرقة ذائبة بالماء تعطي اعلى امتصاص عند طول موجي مقداره ٦١٤ نانوميتر . يشير المنحني القياسي المستقيم للامتصاص مقابل التركيز الى قانون بير يسري ضمن مدى التركيز ٧-٨٤٠ مايكروغرام لايون السيريك في حجم نهائي ٢٥ مللتر (٠,٢٨-٣٣,٦ جزء بالمليون) بامتصاصية مولارية ٤,٥٢ × ١٠^{٣} لتر.مول$^{-١}$.سم$^{-١}$ وحساسية ساندل ٠,٠٣١٠ مايكروغرام.سم$^{-٢}$ وخطأ نسبي اقل من ± ٢,٨% وانحراف قياسي نسبي افضل من ± ٣% اعتمادا على التركيز .

Introduction

The uses of pure cerium are limited, however, misch metal, which is a mixture of rare-earth metals, is used in flints for cigarette lighters and as an additive to remove oxides from cast iron and steel, and as a gas ceramics and carbon industries[1,2].

Various methods have been applied to determination of cerium, these include spectrophotometric[3-4], fluorescence[5] and chromatographic techniques[6] .

This study is designed to establish a new simple, rapid and sensitive colorimetric method for the determination of ceric ion based on the reaction of ceric ion with phenothiazine and sulphacetamide in aqueous solution.

Materials and Methods

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All chemicals used are of analytical grade.

Phenothiazine solution (5 ´ 10^{-4}M): 0.0498 g of phenothiazine was dissolved in 500 ml of ethanol.

Stock ceric ion solution (5 ´ 10^{-3}M): 0.4043 g of cerium(IV) sulphate tetrahydrate was dissolved in 200 ml of 0.5 M sulpuric acid.

Working standard ceric ion solution (5 ´ 10^{-4} M): was prepared by dilution of appropriate volume of stock standard ceric sulphate solution with 0.5 M sulphuric acid.

Sulphacetamide sodium solution (1´10^{-3} M): 0.0509 g of sulphacetamide sodium was dissolved in 200 ml of distilled water.

Procedure: Into a series of 25-ml volumetric flasks, transfer 6 ml of (5×10^{-4} M) phenothiazine. Add 3 ml of 1×10^{-3} M sulphacetamide sodium, followed by increasing volume of acidic solution of (0.5×10^{-4} M) Ce(IV) sulphate. The volum was adjusted to 21 ml with 0.5 M sulphuric acid the solution was diluted to the mark with distilled water and the reaction mixture was allowed to stand for 5 min. The absorbance was measured at 614 nm against blank sample.

Results And Discussion

The influence of various reactions variables were tested to establish the optimum conditions for the proposed procedure and the most suitable values of the variables tested is based on absorbance obtained in each case.

When a very dilute phenothiazine,and sulphacetamide solution is mixed with acidic aqueous solutions of ceric ion , an intense bluish-green dye forms immediately. This dye has a maximum absorption at 614 nm. Fig. (1) shows the spectra of the resulting coloured product and the blank sample.

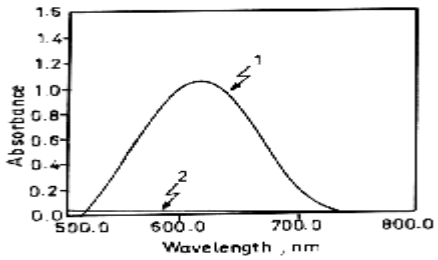


Fig. (1) : Absorption spectra of the product versus blank

When various concentrations of phenothiazine in absolute ethanol are added to a series of 25-ml volumetric flasks and diluted to the mark with distilled water, turbidity is observed in the case of the phenothiazine concentrations to be more than 1.2×10^{-3} M. This may be because the phenothiazine is insoluble in water ; So 6 ml of 5×10^{-4} M phenothiazine in absolute ethanol was found to be optimum and used for the subsequent experiments.

The dye formation reached a maximum with a mole ratio of 1:1 phenothiazine to sulphacetamide sodium. 3 ml of 1×10^{-3} M sulphacetamide sodium was used in all subsequent experiments.

Ce (IV) ion can be used as oxidizing agent in acidic solutions since it forms a precipitate in neutral or alkaline medium[2]. The use of 0.5 M sulphuric acid as a solvent for the Ce(IV) sulphate gives a maximum intensity.

The effect of sulphuric acid concentration on the colour intensity of the dye was studied. A 12 ml of 0.5 M sulphuric acid was found to be optimum and used in the subsequent experiments.

The calibrated flasks were placed in different temperatures ranging from 0 ^{o}C to 70 ^{o}C for 45 minutes. No remarkable change was seen in the absorbance through this range . Therefore, it is recommended to proceed with the reaction at room temperature .

To obtain optimum results, the order of addition of reagents should be followed as given under the recommended procedure.

Maximum colour intensity is reached after the phenothiazine solution has reacted with sulphacetamide sodium and Ce(IV) for 5 min. However, a 5 min. development time was selected as the optimum in the general procedure. The colour obtained was stable for at least 6 hr.

Calibration Curve

When one employs the conditions under recommended procedure, calibration curve of good linearity (correlation coefficient r > 0.9992) for the determination of microgram amount of ceric ion is obtained with a slope of 0.0912 Fig. 2. Beer's law is obeyed over the concentration range 0.28 to 33.6 μg/ml of ceric ions with a molar absorptivity of 4.52×10^3 $l.mol^{-1}.cm^{-1}$ and Sandell sensitivity of 0.0310 $\mu g.cm^{-2}$.

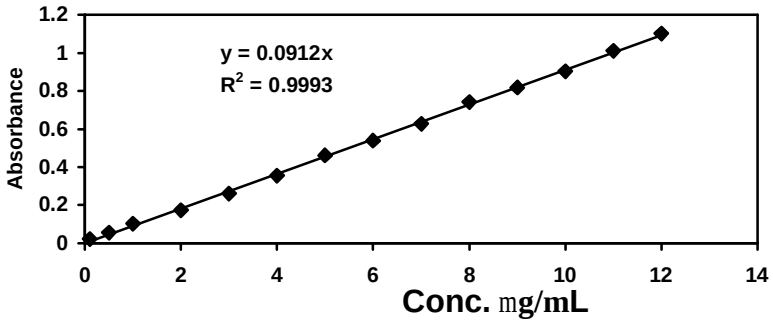


Fig. (2):Absorption spectra of the blank versus water .

Accuracy and precision

To estimate the accuracy and precision of the method, ceric ion was determined at three different concentrations. The results indicate that the present method is accurate and precise (Table 1).

Table (1): Accuracy and precision of the proposed method.

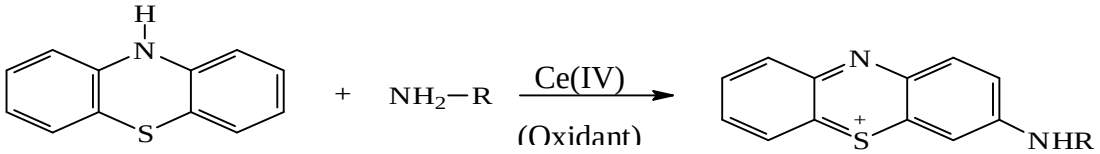
Amount of ceric ion taken ($mg.ml^{-1}$)	Relative error (%)*	Relative standard deviation (%)**
2	+ 2.7	± 2.9

12	- 0.4	± 1.1
22	+ 1.3	± 0.7

* mean of three determinations.
** mean of six determinations.

The nature of the reaction product

The mechanism of the reaction of phenothiazine with sulphacetamide in the presence of cerium(IV) sulphate is not known with certainty, but Al-Talib S.M[7] suggests the following mechanism for the determination of some sulphonamides drugs with phenothiazine in the presence of different oxidizing agents.



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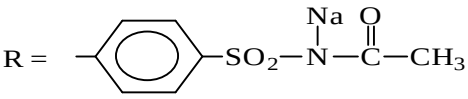

Interference

In general ; Oxidizing materials which react with phenothiazine would be expected to cause a positive interference and reduce materials which react with ceric ion . They would be expected to cause a negative interference in the determination of ceric ion. To show the selectivity of the method, the interfering effects of some cations were examined on determining 150 µg of ceric ion, using the recommended procedure. The result obtained are summarized in Table (2).

Table (2) : Effect of diverse cations on the determination of 150 µg of ceric ion.

Interference	Formatted	Amount of added mg	Interference relative error %
Cd^{2+}	Cadmium chloride	300	- 1.09
Pb^{2+}	Lead acetate	150	Turbid
Cu^{2+}	Copper sulphate	300	+ 3.37
Ba^{2+}	Barium chloride	150	Turbid
Zn^{2+}	Zinc acetate	300	+ 2.66
Ca^{2+}	Calcium chloride	300	+ 2.10
Li^{+}	Lithium carbonate	300	- 1.41

Conclusion

A new simple and rapid colorimetric method has been developed for the indirect determination of small amounts of ceric ion in aqueous solution, based on the using of ceric ion as oxidizing agents in the coupling of phenothiazine and sulphacetamide in acidic medium. The proposed method does not require either temperature control or a solvent extraction step.

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