Spectrophotometric Micro Determination of Ceric Ion using 2, 6 – diamino toluene

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Received: 27/7/2008 ; Accepted: 7/5/2009

Abstract:

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of ceric ion in aqueous solution. The method is based on the reaction of ceric ion with 2, 6- diamino toluene as reagent in acidic solution (0.5 M Sulphuric acid) forming an intense violet colour water – soluble and has maximum absorption at 500 μm. The molar absorptivity was 4.04 x 103 l.mol-1.cm-1 Sandell sensitivities 0.0500. g. cm-2., relative error of ±1.267-0.558% and relative standard deviation of ±0.215-0.086%.

The optimum conditions and the interference of foreign organic compounds have been investigated. The proposed method does not require temperature control or solvent extraction step.

طريقة طيفية مايكروئية لتقدير ايون السيريوم باستخدام 2، 6 - ثنائي أمين تولوين

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ملخص البحث:

تم تطوير طريقة طيفية بسيطة، سريعة وحساسة لتقدير ايون السيريك في محلول مائي. تعتمد الطريقة على تفاعل ايون السيريك مع الكاشف 2، 6 – ثنائي أمين تولوين في وسط حامضي (0.5 مولاري حامض الكبريتيك)، حيث تكونت صبغة بنفسجية ذائبة في الماء تعطي اعلى امتصاص عند طول موجي 500 نانوميتر وكان معامل الامتصاص المولاري 10^3x4.04 لتر. مول$^{-1}$.سم$^{-1}$. ومدى حساسية ساندل 0.500 مايكروغرام.سم$^{-2}$. والخطأ النسبي -1.267±

0.558% والانحراف القياسي النسبي 0.086%-0.215%±. تم دراسة الظروف المثلى وتداخل المواد العضوية الغريبة. الطريقة المطورة لا تحتاج الى ضبط درجة الحرارة أو الاستخلاص بمذيب.

Introduction

It was known that the pure cerium usages are restricted, nevertheless, there is a misch metal which is available as a mixture of scarce – earth metals which has been used in making up or manufacturing the flints of cigarette lighters, and has the ability to be as an addition to purify the steel and cast iron from oxides. Eventually, it can be used in many industries of carbon and as a gas ceramics. [1, 2]

Various spectrophotometrivc methods have been applied for the determination of cerium using methyl thymol blue. (II) [3], (III) [4], N – 4 – chlorophenyl – 2- furohydroxamic acid [5], Solochrome black 6 (BIC. I. Mordant black 3) [6], tetrasulphonated metal phthalocyanane complexes [7], 4- chloro – N – phenyl cinnamohydroxamic acid [8], 4- benaoyl -2, 4- dihydro, 5- methyl-2- phenyl – 3H- pyrazol – 3- one [9], and with tribromo aresenazo by using P_{507} resin separation [10], and by using methyl thymole blue and hexadecylpyridinium bromide [11], and by reaction of ceric ion with phenothiazine and sulphacetamide in aqueous solution [12], [13].

EXPERLMENT

Apparatus:

Absorption measurements were carried out using Digital spectrophotometer PD-303 uv/vis with matched 1-cm optical quartz cells. All measurements were carried out using model 9409 digital. pH meter supplied with an electode type CEI O-12 pH. Weightings were carried out

on balance type Mettler Gp1503S. Heating of solutions were carried out on a water bath of Frost instrument. W_{270k} memmert.

Reagents:

All reagents were of analytical reagents grade.

2,6 diaminotoluene ($5x10^{-4}$M) solution: 0.01221g of 2,6-diaminotoluene (Fluka) was dissolved in 200ml of 0.5M H_2SO_4.

Stock ceric ion (IV) sulphate tetrahydrate ($1x10^{-3}$M) solution: 0.0808 g of cerium (IV) sulphate tetrahydrate (Fluka) was dissolved in 200ml of 0.5M H_2SO_4.

Working standard ceric ion solution ($1x10^{-4}$M): was prepared by dilution of appropriate volume of stock standard ceric sulphate solution with 0.5M sulphuric acid.

Procedure:

Into a series of 25-ml volumetric flasks, transfer increasing volumes of acidic solution of ($0.5x10^{-4}$ M) Ce(IV) sulphate. Add 1ml of 5 x 10^{-4}M 2,6-diamino toluene, the volumes were adjusted to 20 ml with 0.5M sulphuric acid dilute the solution to the mark with ethyl alcohol and allows the reaction mixture to stand for 5min at room temperature.

The absorbances were measured at 500nm against the blank solution.

RESULTS AND DISCUSSION:

Absorption Spectra:

When 40 μg /ml solution of ceric ion is mixed with of 2, 6-diamino toluene an intense violet colour forms immediately. This colour has a

maximum absorbance at 500nm in contrast to the reagent blank which shows no absorption in the visible region Fig(1).

The maximum absorption at 500nm was used in all subsequent experiments.

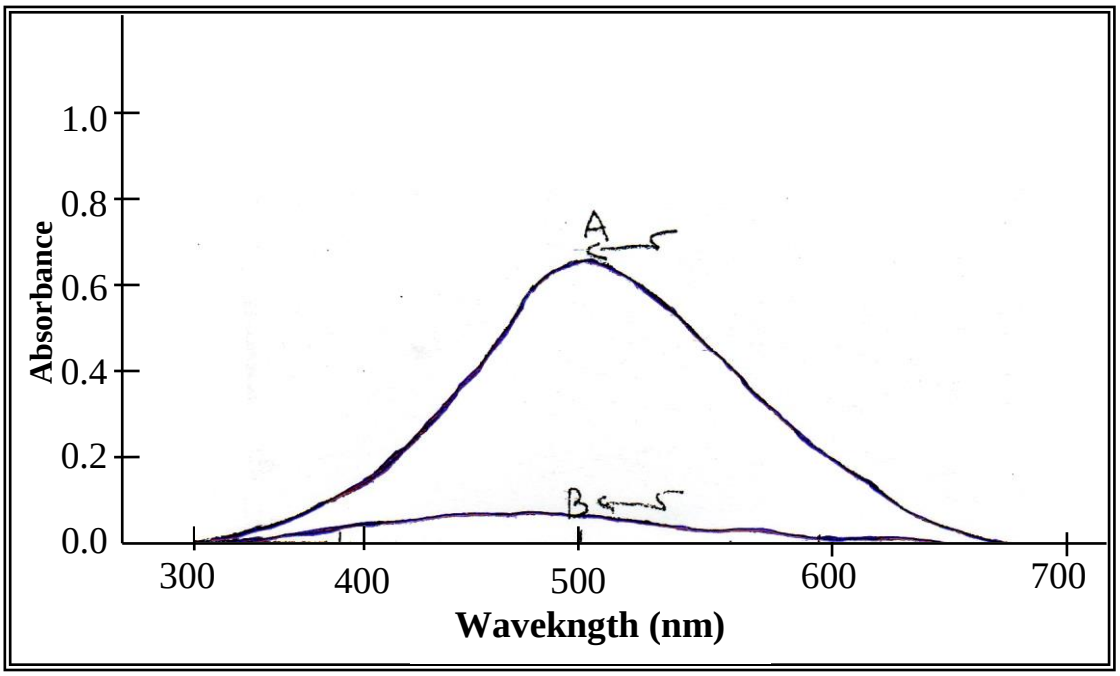


Fig (1): Absorption spectra of (A) 40 μg of ceric ion treated as described under procedure and measured against a reagent blank (B) the reagent blank measured against distilled water.

Effect of Solvent:

The preliminary experiments have shown that ceric ion give coloured product of highest intensity with 2, 6-diamino toluene in acidic medium.Therefore, the reaction has been carried out with different solvent and the results show that the ceric ion give coloured dye with Ethyl alcohol in acidic medium which is recommended in the subsequent experiments Table (1).

Table (1) : Effect of solvent Absorbance / min standing time

Solvent	5	10	15	20	25	30	35	40
Water	0.444	0.425	0.417	0.407	0.388	0.382	0.381	0.374
Ethyl alcohol	0.719	0.716	0.710	0.650	0.611	0.585	0.425	0.418
Acetone	0.478	0.384	0.375	0.358	0.349	0.346	0.340	0.336
Propanol	0.628	0.601	0.530	0.434	0.340	0.335	0.333	0.258
1, 4 Dixan	0.329	0.319	0.310	0.303	0.296	0.275	0.258	0.250

Effect of Reagent Concentration:

The effect of various concentrations of 2, 6-diamino toluene solution $5x10^{-4}$M were studied, and 1ml of this solution was given the highest intensity.Therefore, this volume is recommended in the subsequent experiments. Table (2)

Table (2) : Effect of Reagent Concentration

Volume of $5x10^{-3}$ 2, 6-diamino toluene	**Absorbance**
0.5	0.669
1	0.719
2	0.668
3	0.579
4	0.565

Effect of Sulphuric Concentration:

The effect of various concentrations of sulphuric solution was studied to fixed concentration for maximum colour intensity, the optimum concentration of sulphuric acid solution was 0.5M, whereas it become clear that the reaction does not need acidic control medium, but it could be done without acidic medium at (pH_3). Table (3)

Table (3): Effect of Sulphuric acid Concentration

Sulphuric acid conc. 0.5M	Absorbance VS.Blnk
1	0.352
2	0.330
3	0.720
5	0.723
7	0.725
9	0.721
With out (pH_3)	0.720

Effect of temperature and stability:

The effect of temperature and stabitity on the colour intensity of the dye was studied. In practice, the absorbance was decreased when the colour is developed at Oc^0 or when the calibrated flask is placed in a water – bath at $50c^0$. Therefore, it is recommended that the reaction should be carried out at room temperature ($25c^0$).

It is recommended that the reaction be carried at room temperature as shown in Table (4)

Table (4) : Effect temperature and stability [Absorbance/ Time (min)]

Tem.(C^0)	0	5	10	15	20	25	30	35	40
0	0.215	0.390	0.385	0.377	0.375	0.369	0.340	0.328	0.299
10	0.286	0.563	0.561	0.546	0.538	0.530	0.484	0.467	0.439
Room temp.	0.711	0.720	0.715	0.682	0.670	0.653	0.641	0.628	0.609
40	0.385	0.468	0.459	0.429	0.414	0.410	0.396	0.350	0.355
50	0.209	0.320	0.311	0.303	0.299	0.264	0.258	0.346	0.239

Order of addition of reagents:

To obtain the optimum results, the order of addition of reagent should be followed as given under procedure, otherwise a loss in colour, intensity and stability were observed as shown in Table (5).

Table (5) : The effect of order of addition

Order of addition	Absorbance
2, 6-diamino toluene + ceric ion ceric ion +	0.515
2, 6-diamono toluene	0.718

Calibration Graph:

Empolying the conditions described under procedure, a linear calibration graph, Fig (2) for ceric ion obtained, shows that Beer's law is obeyed over the concentration range (1-40.42) µg per 25ml (0.04-1.61ppm) with a correlation coefficient of 0.9984 slope of 0.0158 and intercept of 0.023.

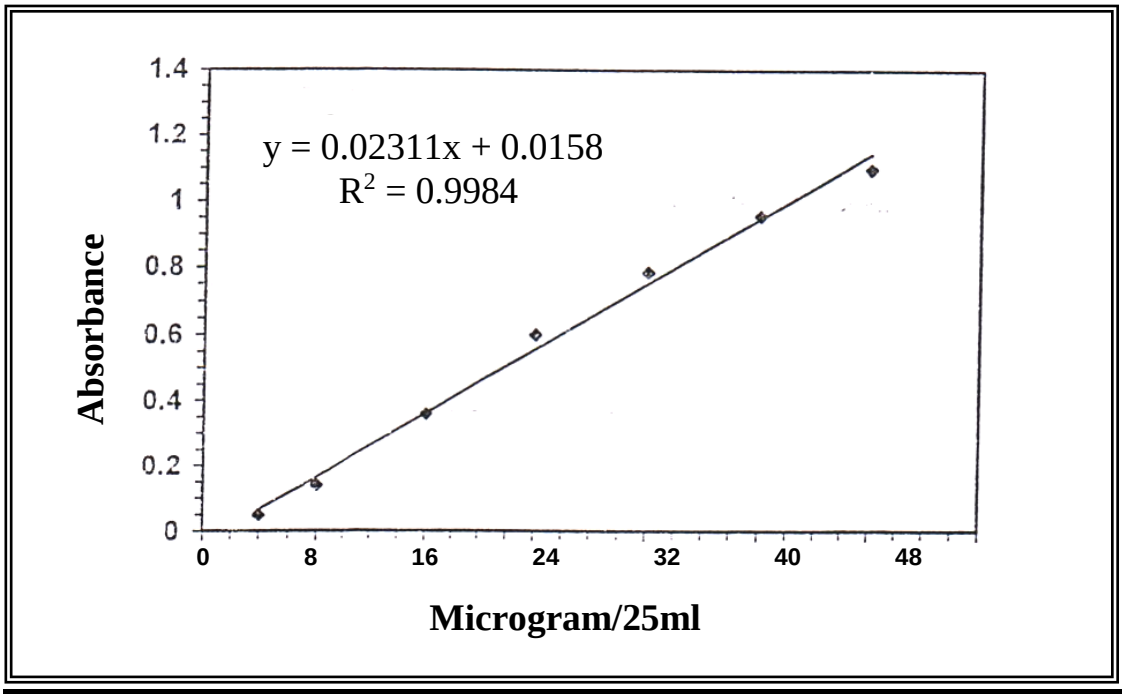


Fig (2): Calibration graph for ceric ion determination using 2.6-dianino toluene reagent

Accuracy and Precision:

To determine the accuracy and precision of the method, ceric ion was determined at three different concentration. The results illustrated in Table (6) indicate that the method is satisfactory.

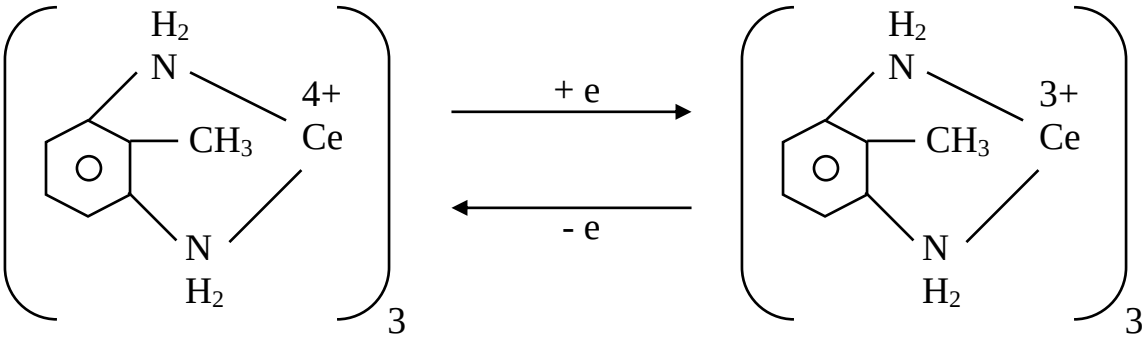
Table (6) : accuracy and precision of the method

Ceric ion μ g/25ml	Relative error %*	Relative standard deviation %*
10	1.267	0.215
20	-0.558	0.086
40	-0.277	0.212

* Average of five determinations.

The nature of the reaction product:

The mechanism of the reaction of ceric ion with 2.6-diamino toluene is not known exactly, but Feigl, Haquenauer- Castro [14], and Wadala, B.A.; Ghazar, H.W. and Soad, F., [15], suggested that cerium ion undergo oxidation – reduction with 2.6-dianino toluene in acidic medium (pale bink) to produce a red – violet dyestuff at 500nm. Therefore, the formation of the dye may probably be occur as follows:



Pale Pink
Oxidized form

Reduced form

Interference:

For the sake of emphasis from the selective method, the influence of many salts and oxidant agents had been studied. However excess of these materials were added alone to 40 µg/25ml of ceric ion using the optimal conditions of estimation.

The obtainable results from table (7) had been enrolled and indicate to selective method and at the same time there is no any noticeable interferences of the salts.

Generally, most of these materials were within the allowable intereferences. (±5%)

Table (7) : Effect of interferences on the determination of 40 µg of ceric ion

Foreign Compounds	Amount added µg	relative error %
Cu^{2+}	200	+2.44
Zn^{2+}	200	+2.50
Ca^{2+}	200	+3.10
pb^{2+}	100	Turbid
Ba^{2+}	100	Turbid
N-chloro succinic amide	200	+1.94

Conclusion:

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of trace amount of ceric ion in aqueons solution based on the oxidative reaction of ceric ion with 2, 6-diamino toluene in acidic medium.

The proposed method does not require neither temperature control nor oxidative agent and buffer solution.

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