



Simple and Selective Determination of Zr (IV) with 1,4-dichloro-2, 5-dihydroxyquinone in a Micellar Solution of Cetylpyridinium Chloride by Zero and Second-Derivative Spectrophotometry

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ABSTRACT

A rapid, simple, selective, and sensitive method for trace determination of Zr (IV) has been developed based on the reaction of 1,4-dichloro-2,5-dihydroxyquinone in a hydrochloric acid medium to form a colored complex which is rendered water soluble by the micellar action of cetylpyridinium chloride (CPC) and measured at λ_{\max} 331 nm. Beer's law is obeyed in the concentration range 0–5 $\mu\text{g}\cdot\text{ml}^{-1}$. The molar absorptivity of the complex, ϵ was found to be $1.6 \times 10^4 \text{ L}\cdot\text{mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity was found to be $5.7 \text{ ng}\cdot\text{cm}^{-2}$. A method for determination of Zr (IV) by second derivative spectrophotometry has also been proposed. The detection limit of Zr (IV) in the derivative method is 6 times lower than that of the zero order method, which shows the higher sensitivity of the derivative method. The method has been applied for determination of Zr (IV) in various samples, and satisfactory results have been obtained.

Keywords: zirconium determination, micellar solution, derivative spectrophotometry

INTRODUCTION

Zirconium occurs in nature as the mineral zircon (ZrSiO_4). Its hardness and useful properties, such as the ability to increase corrosion resistance and mechanical strength of alloys at low and elevated temperature, have made its determination important in special steels and alloys. Also its transparency to thermal neutrons has made zirconium a good construction material

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in nuclear reactors [1, 2]. The direct determination of Zr (IV) in alloy and other samples is of great importance in analytical point of view. There are numerous methods outlined for determination of Zr (IV) in literature [3-9]. Trace amounts of zirconium have been determined by X-ray fluorescence, neutron activation, atomic emission and spectrophotometry (10-15). Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity. Many methods of zirconium determination have been published [1, 3-6, 14-17]. However, some of these methods have both low sensitivity and low selectivity while others have high sensitivity but low selectivity in presence of some ions or molecules. (2,18,19). Arsenazo-III, Alizarin S, pyrocatechol violet and xylenol orange, PAR, Picramine P, Picramine ϵ , Br-PADAP, 5,7-dibromo-8-hydroxylquinoline, 2,2',3,4-tetrahydroxy-3'-sulpho-5'-carboxyazobenzene, 4,5-dihydroxybenzene-1,3-disulfonic acid disodium salt and chrome azurol S have all been proposed to be good ligands for determination of zirconium (15- 18). The determination of zirconium with alizarin S, pyrocatechol violet, and xylenol orange is carried out after separating interfering species. So these methods have low sensitivity and low selectivity [2, 15] Solid-phase spectrophotometry was used to determine trace amounts of Zr(IV) in water, soil, plant materials and ore samples. Zr(IV) was sorbed in a dextran-type lipophilic gel as a complex with 2-(2-benzothiazolylazo)-3-hydroxyphenol [16].

1,4-dichloro-2,5-dihydroxyquinone or Chloranilic acid (CAA) is a well-known precipitating agent for barium, calcium, magnesium, mercury, thorium, lanthanum, etc and in colorimetric determination of anions such as sulfate, chloride, fluoride, EDTA and iodate (18, 19). Metal compounds of the chloranilic acid are almost insoluble in cold water and the color bleaching that accompanies its precipitations have been used as the basis of a colorimetric methods for estimation of these metals [20, 21]. Studies on CAA and its metal complexes have been reported. Some of these reports deal with the structure studies of the complex and the others deal with determination of different species [22, 23]. CAA has been successfully utilized also for spectrophotometric determination of a variety of many organic compounds [29].

Organic micellar media are very useful in analytical applications, including the improved analyte sensitivity in UV-visible spectrophotometric methods and in fluorescence methods and quenching processes. Especially, some surfactants (surface active agents) have been used to improve UV-visible spectrophotometric determination of metal ions with complexing agents. Generally, the metal chelate complexes formed in the surfactant media are more stable than those formed in absence of surfactants [30].

Derivative spectrophotometry offers the advantage of increasing selectivity and sensitivity, compared to normal spectrophotometry. The increased selectivity in derivative spectrophotometry results from the bands that overlap in normal absorption spectra appearing as separated bands in the derivative spectra and derivative mode can eliminate or reduce the effect of much spectral interference. Derivative spectrophotometry can increase sensitivity owing to the amplification of derivative signals and the reducing of noise.

Improvements in selectivity and in sensitivity are easier to obtain when the bands in the normal absorption spectra are fairly sharp [31, 32].

However, in the present method, the use of micellar system avoids the precipitation of Zr (IV) CAA complex and enables the measurements in an aqueous medium, thereby avoiding the extraction steps, while the derivatization of spectral profiles enhances the selectivity and sensitivity of the method.

EXPERIMENTAL

Apparatus

The absorption spectra of solutions were measured using "UV-Visible spectrophotometer Model UV-160A, with a fixed slit width (2 nm), Shimadzu, Tokyo, Japan. This equipment is a double beam recording spectrophotometer and covers the UV-visible range 200-1100 nm.

Reagents

All reagents were of analytical grade, and used without further purification. All of solutions were prepared with fresh double distilled water. Zirconium solution (1000 ppm) was prepared by dissolving 0.390 g $ZrOCl_2 \cdot 8H_2O$ in 5 mL conc. HCl and diluting to 100 ml with 2M HCl. 0.1 % (w/v) solution of CAA was prepared by dissolving 0.25 g CAA (Aldrich) in 250 ml fresh double distilled water. The surfactants used were sodium dodecylsulfate, triton X-100, cetyltrimethylammonium bromide, and cetylpyridinium chloride which were Merck production.

Analytical Procedures

Ordinary spectrophotometry

An aliquot of the sample solution containing not more than $5 \mu\text{g ml}^{-1}$ Zr (IV) was transferred into a 10 ml capacity standard measuring flask, then 1.5 ml of HCl was added to give a final concentration of 1.81 M, 2 ml 0.1 % (w/v) CAA reagent solution and $150 \mu\text{l}$ 2 % (w/v) CPC solution were added. The volume was made up with fresh double distilled water. The solution was allowed to stand for 5 min after mixing. The absorbance of Zr (IV)-CAA complex was measured at 331 nm against a reagent blank. The measurement was made in 1-cm quartz cells.

Second-derivative spectrophotometry

When the Zr (IV) content of the colored solution prepared by the above procedure is too low ($0.08 - 4.0 \mu\text{gml}^{-1}$ Zr (IV)), the second-derivative spectrum from 300-400 nm was experimented. The second -derivative spectrum is obtained for a $\Delta\lambda$ (N) value of 9 nm and scan speed of 1500 nm/min. The analytical signal is obtained by measuring the distance from

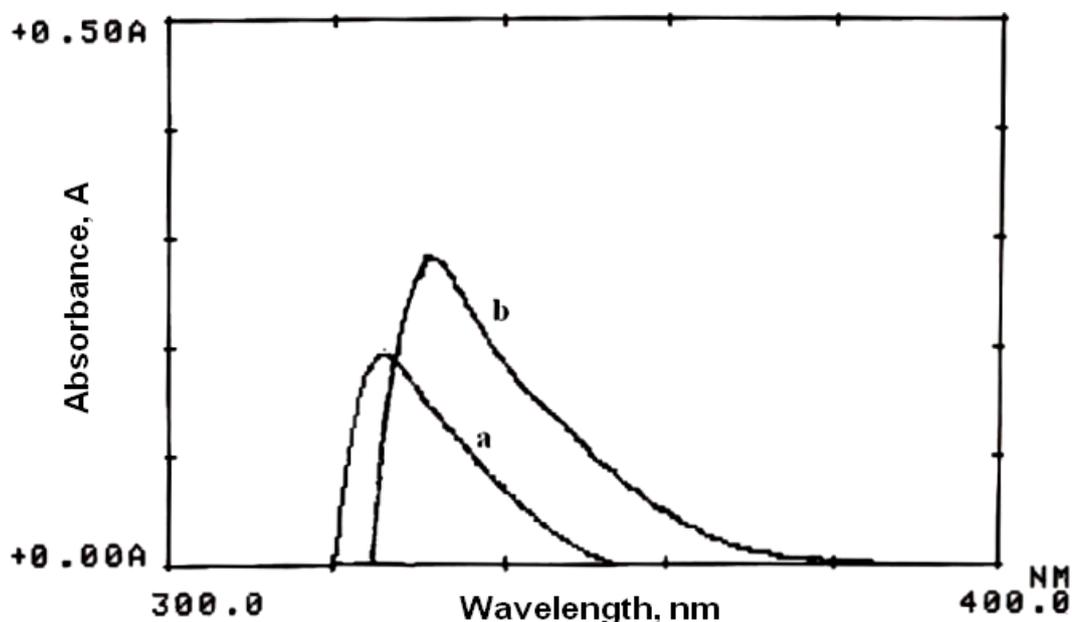


Figure 1. Absorption spectra of Zr (IV) –CAA (a), Zr (IV) -CAA-CPC (b) complexes against reagent blanks. [Zr] of 1.5 ppm, 2 ml of 0.1% CAA, 150 μ L of 2 % CPC in 1.8 M HCl

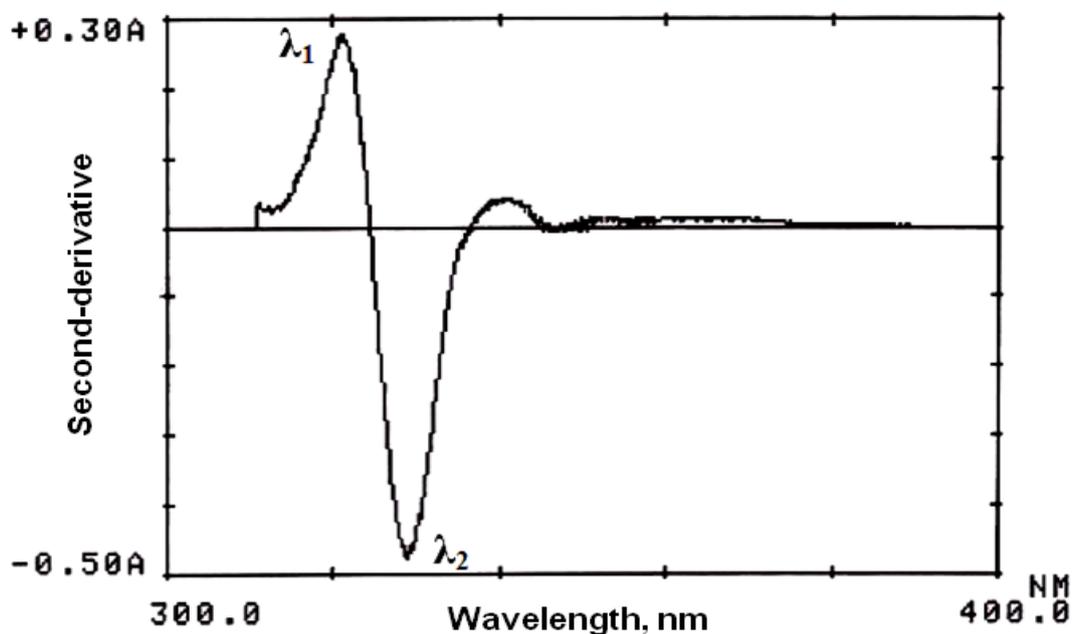


Figure 2. Second derivative spectrum of Zr (IV)-CAA-CPC complex at the same condition in [Figure 1](#)

λ_1 to λ_2 . Zr (IV) contents were determined by comparing the values with an appropriate calibration graphs.

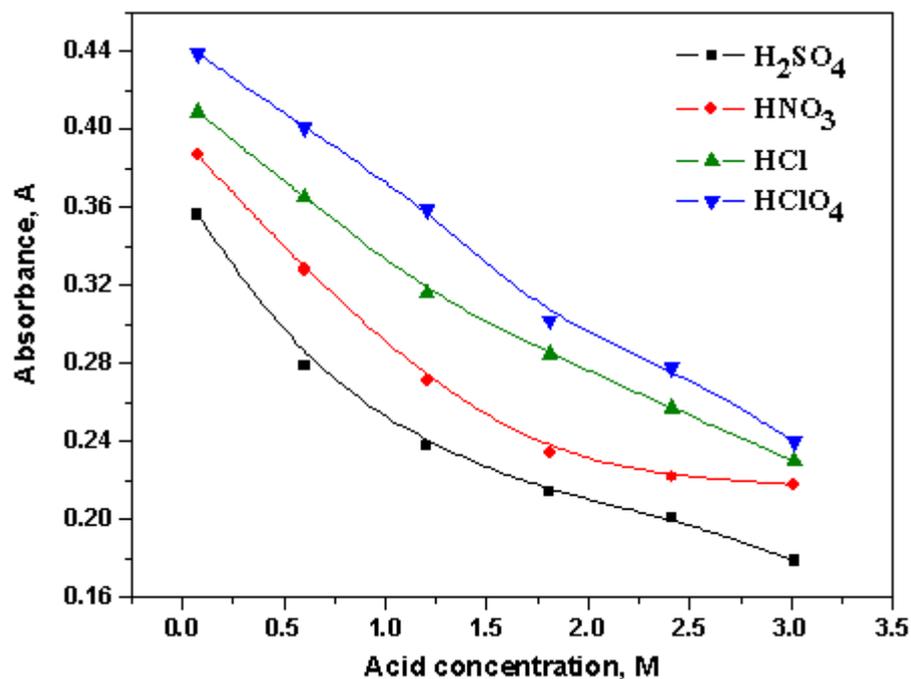


Figure 3. Effect of various acids on absorbance of the Zr (IV)-CAA complex

RESULTS AND DISCUSSION

Absorption Spectra

The reagent 1,4-dichloro-2, 5-dihydroxyquinone (CAA) reacts with zirconium (IV) ion in acidic media to form a colored complex in aqueous solution at ambient ($25 \pm 1^\circ\text{C}$) temperature. **Figure 1** shows the absorption spectra of Zr (IV)-CAA complex in absence and presence of CPC as a cationic surfactant under the optimum conditions at 326 and 331 nm, respectively. The color formation reaction in presence of CPC was more stable and exhibited a higher absorbance in comparison that in absence of CPC. Moreover, the proposed procedure can be further sensitized by employing the derivative spectroscopic technique. The use of derivative spectroscopy is not only simple and sensitive but also improves the selectivity.

A study of the first, second, third and fourth derivative spectra of the zirconium complex in surfactant media under the optimum conditions demonstrated that the second derivative spectra offers better sensitivity and selectivity compared to other derivative spectra and hence was chosen in subsequent investigations, **Figure 2**. In the present work a peak to peak method between $\lambda_1 = 322$ and $\lambda_2 = 329$ nm was applied.

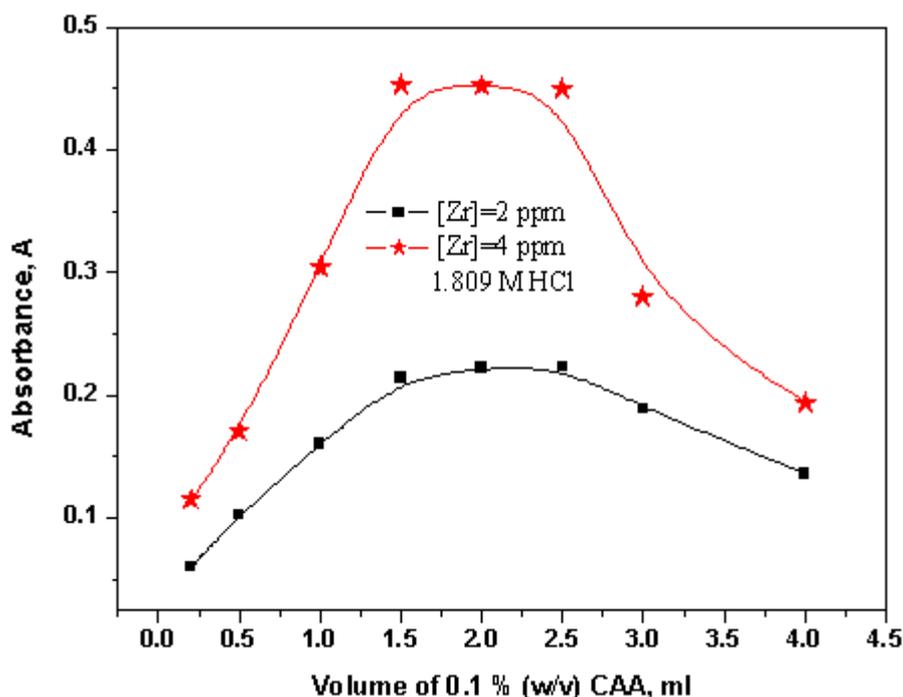


Figure 4. Effect of CAA concentration on absorbance of Zr (IV)-CAA complex

Effect of acidity and acid type

The selection of acidic medium for formation of colored complex between CAA reagent and low concentrations of highly charged metal ions is of special analytical interest. Irreproducibility in Zr (IV) measurements due to hydrolysis and polymerization is minimized under such conditions, where hydrolysis of zirconium ions occurs at pH from 1 to 5.5. Different concentrations (0.08 – 3.0 M) of HClO₄, HCl, HNO₃ and H₂SO₄ were tried as acidic media for complexation. It was found that H₂SO₄ reduces the absorbance of the zirconium complex at 326 nm. This may be as a result of complex formation between SO₄²⁻ and Zr (IV). The absorbance of Zr (IV) complex in HNO₃ is small in comparison to HCl and HClO₄. Absorbance of complex in HCl is close to that in HClO₄. Therefore, HCl was used as acidic media because of its lower cost.

The effect of acids concentration on absorbance signal of Zr (IV)-CAA complex was tested with 2.5 µg/ml Zr (IV), **Figure 3**. It is clear from this figure that the absorbance of the zirconium complex increases with decreasing acids concentration with a maximum absorbance at about 0.08 M acidity. However, the lower acidities also enhance the interference caused by other ions. Therefore, 1.8 M HCl is used in all studies as acidic media to minimize interferences and polymerization.

Table 1. Effect of different surfactants on the Zr (IV)-CAA complex

Surfactant	Surfactant Type	λ_{\max} , nm	Absorbance	Molar absorptivity, $L \cdot mol^{-1} \cdot cm^{-1}$
Without	-----	326	0.15	9.1×10^3
CPC	cationic	331	0.271	1.57×10^4
CTAB	cationic	329.5	0.25	1.5×10^4
SDS	anionic	327	0.16	9.7×10^3
Triton X-100	non ionic	326	0.15	9.1×10^3

Effect of reagent concentration

Since CAA is the complexing agent that reacts quantitatively with the analyte, optimization of its concentration is very important. The effect of CAA concentration on absorbance of Zr (IV)-CAA complex at 2 and 4 $\mu g/ml$ Zr (IV) in 1.8 M HCl was examined by measuring the absorbance at 326 nm of solutions containing a constant concentration of Zr (IV) and varying amount of the reagent.

The maximum and constant absorbance was obtained at the range 1.5 – 2.5 ml of 0.1% (w/v) CAA reagent solution. The absorbance decreased after that, as shown in [Figure 4](#). Therefore, 2 ml of 0.1 % (w/v) CAA reagent solution in a final volume of 10 ml was selected.

Effect of surfactant system and surfactant concentration

When the aqueous CAA reagent is added to zirconium solution, the violet colour of the complex directly appears. After about 3 min the solution becomes turbid and the complex is precipitated after that. Surfactants, on dissolution in water, form organized molecular assemblies called micelles. The structure of the micelle is such that the polar head groups are in contact with the bulk aqueous solution, while the hydrophobic chains are directed inside the micelles performing a nonpolar core, that enhances the solubility of organic compounds in water⁽³³⁾. This phenomenon of micellar solubilization has been used in the development and modification of different methods of analysis⁽³³⁾. Since a surfactant should be used as a solubilizing agent, various surfactants were tried to overcome the precipitation of Zr (IV)-CAA complex. The effect of various surfactants such as Triton X-100 (neutral surfactant), sodium dodecyl sulphate, (SDS) (anionic surfactant), CPC and cetyltrimethylammonium bromide (CTAB) (cationic surfactants) on the absorption profiles of the system has been investigated, [Table 1](#).

In presence of the cationic surfactant CPC and CTAB, the complex exhibited its maximum sensitivity. The reaction between Zr (IV) and CAA was studied in presence of different concentrations of CPC and CTAB solutions. The effect of CPC and CTAB concentration on the absorbance of 2 $\mu g/ml$ Zr (IV) is shown in [Figure 5](#).

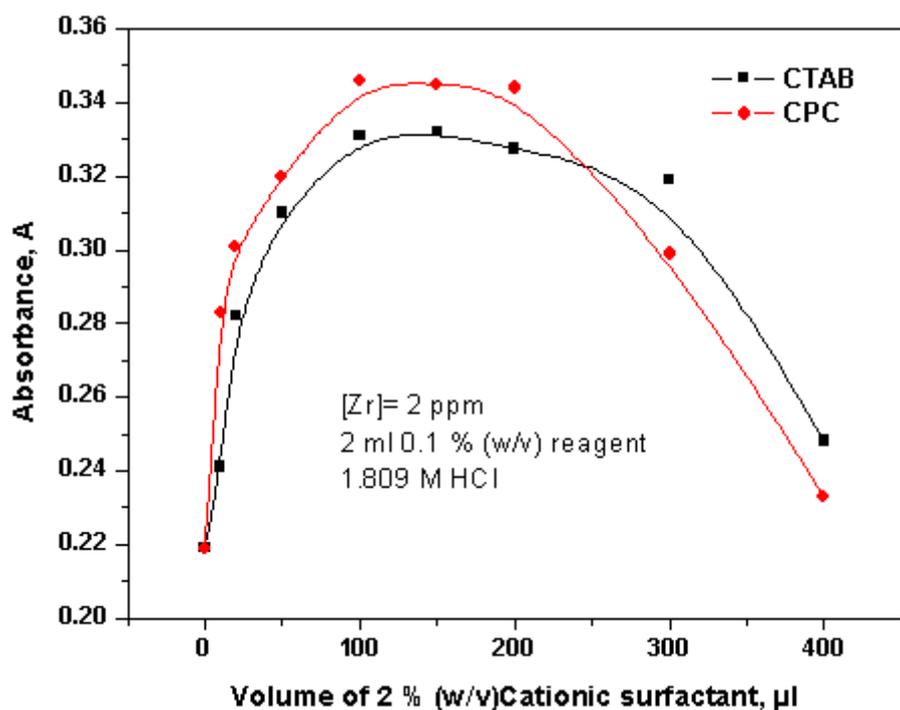


Figure 5. Effect of CPC and CTAB concentrations on absorbance of Zr (IV)- CAA complex

It is clear that the absorbance is slightly higher in case of using CPC compared to that of CTAB. It was found that the absorbance of Zr (IV)-CAA complex reaches its maximum value at the range from 50 to 200 μl of 2 % (w/v) CPC solution. Hence CPC has been selected to improve the sensitivity and stability of the colored complex and 150 μl of 2 % (w/v) CPC was found to be optimum for this analytical work.

Effect of standing time and temperature

The influence of time on formation of Zr (IV)- CAA complex was also studied at the optimal working conditions. It was observed that, the absorbance value of Zr (IV) complex solution becomes maximum and constant after 5 min as shown in **Figure 6**. Therefore, a 5 min of standing time was selected for all measurements. The absorbance value of Zr (IV)-CAA complex remained stable and constant for 9 h at least in surfactant media at ambient ($25 \pm 1^\circ\text{C}$) temperature. The absorbance was found to be temperature independent in the range 15- 40 $^\circ\text{C}$. Above 40 $^\circ\text{C}$, the absorbance gradually decreases with a rise of temperature.

Optimization of variables

Derivative spectrophotometry is extremely effective for enhancing the sensitivity and selectivity of ordinary (zero-order spectra) spectrophotometry. Beside the chemical parameters which affect the complex formation and enhancement of sensitivity and selectivity

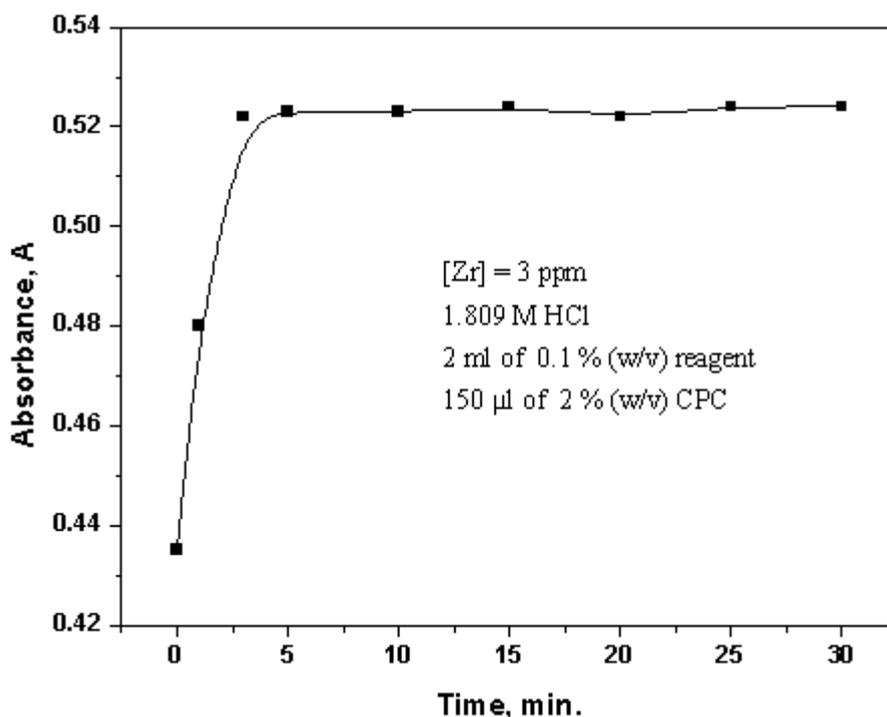


Figure 6. Effect of standing time on absorbance of Zr (IV)-CAA-CPC complex

Table 2. Optimization of the different parameters

Variable	Range studied	Optimum value
Chemical		
Conc. HCl, M	0.0753 – 3.015	1.80
0.1 % (w/v) CAA, ml	0.2 - 4.0	2.0
2 % (w/v) CPC, µl	0 - 400	150
Spectral		
Derivative order	0 - 4	2
$\Delta\lambda$ (N), nm	1 – 9	9
Analytical wavelength, nm	300 - 400	331*, 322-329 #
Scan speed, nm / min	480 - 2400	1500

*) λ_{max} in normal mode

#) distance between $\lambda = 322$ and $\lambda = 329$ nm in derivative mode

of the obtained normal spectra there are also some instrumental parameters, which affect the shape of the derivative spectra. These mainly include derivative order, the wavelength scanning speed, $\Delta\lambda$ and smoothing factor of the derivative spectra. These parameters need to be optimized to give a well-resolved large peak i.e. to give good selectivity and higher sensitivity in the determination process. The overall parameters (chemical and spectral) are shown in **Table 2**.

Table 3. Precision and accuracy of Zr (IV) determination methods

Zirconium taken ($\mu\text{g}/\text{ml}$)	Zirconium found ($\mu\text{g}/\text{ml}$)			
	Normal spectrophotometry	Error, %	Derivative spectrophotometry	Error, %
0.1	---	---	0.100 ± 0.002	0.0
0.5	0.503 ± 0.004	0.60	0.5024 ± 0.004	0.48
2.0	2.014 ± 0.02	0.70	2.000 ± 0.020	0.00
2.5	2.498 ± 0.012	0.08	2.480 ± 0.010	0.80
3.0	3.040 ± 0.002	1.33	3.020 ± 0.002	0.67
4.0	4.030 ± 0.033	0.75	3.981 ± 0.020	0.48

\pm) are standard deviation of six replicate analyses

Calibration graph, precision and sensitivity

The calibration curves for the determination of zirconium in the standard solutions of zirconium ion were constructed according to the general procedure under the optimum conditions developed above. It was observed that in case of zero order method, Beer's law is obeyed in the concentration range up to $5 \mu\text{g}/\text{ml}$ zirconium. The optimum concentration range taken for determination of zirconium was $0.5 - 5 \mu\text{g}/\text{ml}$. The data was found to fits the equation:

$$A = 0.02189 [\text{Zr}] + 0.16495 \quad (R = 0.9981)$$

The molar absorptivity (ϵ) and Sandell sensitivity (S) calculated from the above equation were $1.65 \times 10^4 \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and $0.0055 \mu\text{g}\cdot\text{cm}^{-2}$, respectively.

In the second derivative mode, the calibration graph prepared by plotting the distance value between $\lambda_1 = 322$ and $\lambda_2 = 329$ nm versus Zr (IV) concentration was found linear over the range $0.08 - 4.0 \mu\text{g}/\text{ml}$ Zr (IV). This indicates that the detection limit of Zr (IV) in the derivative method is 6 times lower than that of the zero order method which shows the higher sensitivity of the derivative method. The data fits the equation,

$$d^2A/d\lambda^2 = 0.015 [\text{Zr}] + 0.48646 \quad (R = 0.9996)$$

Where A is the absorbance of Zr (IV)-CAA-CPC complex at 331 nm, $d^2A/d\lambda^2$ is the second derivative value between $\lambda_1 = 322$ and $\lambda_2 = 329$ and [Zr] is the concentration of zirconium ion in $\mu\text{g}/\text{ml}$.

The derivative method is more sensitive than the normal spectrophotometry, and the derivative plot gives a higher sensitivity and thus it is recommended for Zr(IV) determination in different samples. Precision of this method was tested with different solutions of Zr (IV), **Table 3.**

Table 4. Effect of foreign ions on determination 1 $\mu\text{g}\cdot\text{ml}^{-1}$ of Zr(IV) using CAA in micellar medium

Interfering ion	Limiting mass ratio (Zr: interfering ion)	
	Ordinary	Second-order
K (I)	1:1000	1:1500
Ca (II)	1:170	1:200
Sr (II)	1:100	1:120
Mg (II), Ba (II)	1:260	1:300
Cu (II), Cr (III), Co(II), Pb (II), Zn (II)	1:90	1:120
Mn (II)	1:60	1:90
Fe (II)	1:220	1:270
Al (III)	1:260	1:300
Gd (III), Sm (III), Eu (III)	1:80	1:85
Fe (III)	1:100	1:120
Si (IV)	1:50	1:65
Ti (IV)	1:25	1:22
Hf (IV)	Interference	Interference
Mo (VI)	Interference	Interference
Citrate, Oxalate	1:900	1:950

Effect of foreign ions

Under the optimum conditions given in **Table 1**, the effects of various foreign ions on determination of Zr (IV) with CAA reagent in CPC micellar medium solution have been investigated. **Table 4** shows the tolerable amounts of the examined ions in determination of 1 $\mu\text{g}\cdot\text{ml}^{-1}$ Zr(IV) by zero order (normal spectrophotometry) and second-derivative spectrophotometry. An amount of an ion in $\mu\text{g ml}^{-1}$ that will produce $\pm 3\%$ change in absorbance was taken as the tolerance limit.

From **Table 4**, it was found that, determination of zirconium with CAA method has a large tolerance limit in comparison to other methods because the acidity of reaction media increases the tolerability of many ions and prevent them from complexation with CAA. Many of these ions interfere in determination of zirconium with other methods. The only series interference from hafnium and molybdenum which form similar complexes with CAA at this condition must be removed before determination. The influence of foreign ions on the second-derivative method was compared with the normal spectrophotometry. Second-derivative spectrophotometry shows better selectivity than the normal spectrophotometry. Thus, second -derivative spectrophotometry is more suitable for direct determination of Zr (IV) using CAA as a reagent in CPC micellar medium.

Comparison with other methods

Most of colorimetric methods for Zr (IV) determination required a prior separation steps and somewhat time-consuming (2, 15) and some of them require some care in pH adjustment for sensitivities comparable to those obtained with CAA method. A comparative

Table 5. Comparison of reagents for spectrophotometric determination of microamounts of zirconium

Reagents	Acid conc. Or pH	Effective range in ($\mu\text{g/ml}$)	Sensitivity (ng/cm^2)	Ref.
Solochrome azurine BS	---	---	8	34
Nitroalizarin	---	---	7	34
Ferron	---	---	6	34
4-(2-pyridylazo)-resorcinol	2.5	0.5 - 5.0	1.3	34
Alizarin red S	---	---	13	4
Alizarin red S	1 M HCl	1.0 - 17	---	5
Alizarin red S	2.3	0.5 - 20	---	4
Alizarin red S	2.5	5.0- 200	---	1
Chloroiodo oxine	---	----	5.8	34
HTC ^a	5.0	0.0 – 2.0	3.4	34
		0.4 – 4.0	5.1	
2,4.DHBINH ^b	1.5	0.18- 4.56 *		35
CAA	1.81 M HCl	0.5 - 5.0	5.5	this work
		0.08 – 4.0 #		

^a) Is 3-hydroxy-2-(2-Thienyl)-4H-Chromon-4-one.

^b) Is 2, 4-dihydroxy benzaldehyde isonicotinoyl hydrozone.

^{*}) by first derivative spectrophotometry method

[#]) by second derivative spectrophotometry method

evaluation of the proposed method with some of the reported ones for determination of zirconium is given in **Table 5**. It is observed that in case of the present method using CAA in micellar medium not only the sensitivity is better but also the selectivity is better than the widely used methods.

Analytical Application

The present procedure was applied for determination of zirconium in aluminum alloy, waste water collected from our laboratories and simulated sample. The simulated samples were prepared by combining zirconium (IV) standard solution with appropriate amounts of most interfering foreign ions. The composition of alloy in % is :Zr (IV) = 0.033 – 0.310 , Mn (II) = 0.08-1.5, Ti(IV) = 0.040-0.30, Be(II) = 0.004 -0.1, Si(IV)= 0.12-8.5, Zn (II) = 0.18-1.0, Fe(III) = 0.07-0.5, Cu (II) = 0.01-7.0, Al (III) = 89-92. The simulated samples contained 2 ppm Zr (IV), 10 ppm Cu(II), 12 ppm Cr(III), 5 ppm Co (II), 5 ppm Cd (II), 50 ppm Ca (II), 5 ppm Al (III), 5 ppm Sm (III) and 2 ppm Fe (III). The zirconium contents in the above samples were determined by the recommended procedure and the results are listed in **Tables 6** and **7**. It can be seen that the results by the recommended procedure are in accordance with the certified values and show that this method has a good accuracy and is applicable for routine measurements.

Table 6. Determination of Zr (IV) in aluminum alloy by the second- derivative spectrophotome

Aluminum Alloy Conc., ppm	Zr(IV) Found* (ppm)	Recovery , %
Zr (IV) = 1.0, Mn (II) = 3.0 Ti (IV) = 2.0, Be (II) = 1.0 Si (IV) = 4.0, Zn (II) = 6.0 Fe (III) = 3.0, Cu (II) = 1.0 Al (III) = 287	1.04 ± 0.02	104

*) average of three determination

Table 7. Determination of Zr (IV) in wastewater and simulated samples by the second derivative spectrophotometry

Sample No.	Spiked Zr (IV) (ppm)	Zr (IV) Found* (ppm)	Recovery , %
No. 1	1.0	0.960 ± 0.017	96.0
No. 2	2.0	1.930 ± 0.010	96.5
No. 3	3.0	2.927 ± 0.008	97.6
No. 4	4.0	3.921 ± 0.005	98.0
Simulated sample	2.0	2.028 ± 0.009	101.4

*) average of three determination

CONCLUSION

The method using 1,4-dichloro-2, 5-dihydroxyquinone(CAA) as a spectrophotometric reagent to determine zirconium in presence of CPC as a surfactant is selective, rapid and simple. The zirconium-CAA-CPC complex is stable and the sensitivity is comparable to the other analytical methods. A method for determination of zirconium by the second derivative spectrophotometry has also been proposed. The detection limit of zirconium in the derivative method is 6 times lower than that of the zero order method, which shows the higher sensitivity of the derivative method. This method was successfully applied to determine zirconium in various samples, and satisfactory results have been obtained. In addition, the method involves less sophisticated instrumentation.

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