SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM USING CHROME AZUROL S (CAS) AS COMPLEXING AGENT IN AQUEOUS STREAMS OF NUCLEAR FUEL REPROCESSING

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Abstract

A sensitive and reproducible method for the direct spectrophotometric determination of zirconium is reported. The method is based on zirconium forms a stable bluish violet colour complex with Chrome Azurol S (CAS) which has maximum absorption at 598 nm at pH 4.2. The complex obeys Beer's law in the concentration range of 1-7 µg/mL. Detection limit, molar absorptivity and Sandell's sensitivity were 2.42 µg/mL, 3.93 x10^{3} L.Mol^{-1}.cm^{-1}and 2.54 x 10^{-4} µg/cm^{2} respectively. Relative standard deviation is less than 2% and correlation coefficient is 0.997. The present method is highly sensitive, selective, rapid and simple. It is directly applicable for the determination of zirconium in environmental, industrial, water and nuclear reprocessing samples.

Keywords
Zirconium, Chrome Azurol S, molar absorptivity, Acetate buffer.

1. INTRODUCTION

Zirconium is widely distributed in earth's crust [1]. It has many useful properties such as ability to increase corrosion resistance and mechanical strength of alloys at low and elevated temperatures. It is highly active metal but, like aluminium, has a tendency to form a stable cohesive protective oxide films. It is mostly used in ceramic industry, refractories, glazes, enamels, foundry mold and abrasive grits. It is used for removing sulphur, nitrogen and oxygen from steel and in the copper manufacturing. Also, its transparency to thermal neutrons has made zirconium a good structural material in nuclear reactors and chemical plants [2]. In the reprocessing of Fast Breeder Reactor (FBR) nuclear fuel zirconium is of particular importance because it is one of the most readily extractable long lived fission products and contaminates uranium and plutonium products. The fission yield of Zr is 7-7.5%. ^{95}Zr has a half-life of 65 days and is in transient equilibrium with ^{95}Nb half-life 35 days, 765.79 keV γ with 100% intensity. ^{95}Zr is to be considered while designing the solvent extraction flow sheet while reprocessing the fuels with a cooling period of around two years or so. The ^{95}Zr - ^{95}Nb pair is responsible for the majority of gamma activity of dissolver solution of short cooled fuels and it contributes to around 1% of the total activity for a typical FBR fuel with 6 month's cooling period.

Determination of trace amounts of zirconium in environmental and industrial samples is interesting because of the high toxicity of its compounds. There are numerous analytical methods for quantitative determination of zirconium outlined in the literature. Different spectroanalytical techniques such as molecular fluorescence spectrophotometry [3], atomic absorption spectroscopy (AAS) [4], laser ablation inductively coupled plasma optical emission spectrometry (LAICP-OES) [5], X-ray fluorescence spectroscopy (XRF) [6-7], induced plasma atomic emission spectrometry (ICP-AES) [8-11], and UV-Vis spectrophotometry [18-37].

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Other techniques such as neutron activation [12], polarography [13-15], high performance liquid chromatography (HPLC) [4], liquid chromatography [16-18], and chelating ion exchange followed by spectrophotometric detection [17] were also reported. UV-Vis spectrophotometric methods have been widely used due to simplicity, rapidity, low costs and wide applications [19-21]. For this purpose, widely-used chromogenic reagents are pyrocatechol violet [23], alizarin red S [24-26], arsenazo I and III [27-29], xylenol orange [17,30-33], Janus Green dye [34], 2,4-dinitrophenol- (6-azo-2)-1-napthol- 3,8-disulphonic acid (picramine ε) [35], 4-(2-pyridiylazo) resorcinol (PAR) [36-37], 2-(6-bromo-2-benothiaoylazo) 5-diethylaminophenol and sodium lauryl sulphate [38], 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol [39], 5,7-dibromo-8-hydroxyl quinoline [40], Chorme azurol s [41], for determination of Zr(IV) by spectrophotometry was reported. Some methods have low sensitivity and selectivity and others have high sensitivity but low selectivity. Table 1 represents the comparison of some spectrophotometric methods for the determination of zirconium. In the present paper, a sensitive spectrophotometric method for quantitative determination of zirconium, based on its complex formation with chrome azurol S at pH 4.2 is described.

2. EXPERIMENTAL

2.1. Apparatus

All absorbance measurements were recorded by indigenously developed fiber optic aided spectrophotometer with dip type probe. Chemlabs, Bangalore, make Micro-07; pH/mV meter coupled with glass electrode was used for pH measurements.

2.2. Reagents and Chemicals

All the reagents used were of analytical grade and all solutions were prepared using distilled water. A standard zirconium solutions (100$\mu g/mL$) were prepared by dissolving ZrO $(NO_3)_2 \bullet 2H_2O$, (Lobal Chemie) in distilled water. The solution was standardized as per standard procedure [42]. Working solutions were prepared by appropriate dilution. Buffer solutions were prepared by using sodium acetate (0.1M) and acetic acid (0.1M) and pH adjusted to 4.2 with 0.05M acetic acid. Stock solution of Chrome Azurol S (CAS) was prepared by weighing 0.05 g (BDH) in 100 mL standard flask and diluted with water.

2.3. Procedure

A suitable aliquot of Zr (IV) solution was transferred quantitatively into a series of 10 mL capacity standard flasks, then 1 mL of sodium acetate /acetic acid buffer, 0.3 mL of 0.05% Chrome Azurol S were added. The mixture was then made up to the mark with distilled water and 1M nitric acid. Absorbance was measured against a reagent blank prepared under identical conditions at 598 nm.

3. RESULTS AND DISCUSSION

The structure of chrome azurol s and reaction with zirconium for the spectrophotometric detection are shown in figs.1 & 2. The standardized spectrophotometric procedure for zirconium shows a linear calibration graph over a range of 1-7 µg/mL with a correlation coefficient of 0.997 (7 replicates). Figure 3 shows the calibration graph obtained with maximum absorbance at 598 nm for standard zirconium solution. In the present study, chrome azurol S is a preferred chromogenic reagent on account of its high sensitivity and selectivity. The Zr-CAS complex formed is stable. Typical absorption spectra of chrome azurol s and zirconium at pH 4.2 at 598 nm are shown in fig. 4.

Table 1 summarizes the optimum experimental conditions for the quantitative determination of zirconium with chrome azurol s. The reaction conditions, as well as the various experimental parameters affecting the formation and stability of the bluish violet coloured complex Zr-CAS, were carefully investigated and optimized. The minimum time required for complete colour development of Zr-CAS complex at pH 4.2 is found to be 5 min and the developed colour retained for more than 24 *hours*. The results obtained by present method are in good agreement with those obtained by the spectrophotometric technique [39] with BrPADAP as a chromogenic reagent and represented in table. 2.

3.1 Effect of chrome azurol s

It was observed from the experimental studies that minimum quantity of 0.05% of CAS is needed for effective determination of zirconium. In this study, the different volumes of 0.05% of CAS were added to the solution containing constant volume of 1 *mL* of buffer and fixed concentration of zirconium. The obtained results are shown in fig 5. From this, it is observed that 0.3 *mL* of 0.05% CAS is enough to determine the zirconium. When higher volumes of CAS were added, there was a sharp decrease in absorbance and further addition lead to no change in absorbance measurements.

3.2 Effect of Buffer solution

The effect of addition of buffer solution for the determination of zirconium is presented in Figure 6. From this, it was found that 1 *mL* of buffer is sufficient and even if the volume of buffer solution is increased beyond 1 *mL*, there is no difference in absorbance measurements.

3.3 Effect of interference and masking agents

Effect of interfering species such as UO_2^{2+}, Gd^{3+}, Sr^{+} and Rb^{+}, on the determination of zirconium was studied. Some interfering species were masked using ascorbic acid or EDTA. The metal ions such as UO_2^{2+}, Gd^{3+}, Sr^{+} and Rb^{+} do not interfere with the determination of zirconium in concentrations up to 50 ppm. Figure.7 represents the spectrum of zirconium and mixture of zirconium and uranium. From this, it clearly indicates that no interference of uranium during the analysis of zirconium using CAS was observed.

3.4 Analytical applications

The efficiency of the developed method for the spectrophotometric determination of zirconium in simulated samples were established by comparing the results with those obtained with zirconium concentration estimation by Zr-BrPADAP method [39]. The results are represented in Table 2 and are found to be in good agreement. The present method is also comparable with various published methods as shown in (Table 1).

4. CONCLUSIONS

A modified spectrophotometric method for the determination of zirconium with CAS has been developed. This reagent forms a very stable complex with zirconium at pH 4-5. The proposed method is simple, rapid, reliable and accurate. The method possess distinct advantages over existing methods in cost, simplicity, easy operation, good sensitivity and potential for application to the determination of zirconium in environmental, industrial and nuclear reprocessing samples.

Table 1 Comparison of some reagent for spectrophotometric determination of zirconium with the published methods

Reagents	λ_{max} (nm)	ε ($L.Mol^{-1}.cm^{-1}$)	Remarks	Ref.
Xylenol Orange	429	6.9×10^5	Extraction with n Hexane	[33]
Janus Green Dye	606	-	Catalytic oxidation by BrO_3^-	[34]
4-2-(pyridylazo)-resorcinol (PAR)	530	6.6×10^4	Uranium is interfere	[36-37]
Aresnazo III	665	1.5×10^4	Uranium is interfere	[38]
2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol (Br-PADAP)	585	1.5×10^5	Methanol–water mixture	[39]
5,7-dibromo, 8-hydroxyquinoline	416	1.05×10^4	Extracted with $CHCl_3$	[40]
Chrome Azurol S	598	3.93×10^3	Extraction is not required, uranium is not interfere	Present method

Table2 Spectral characteristics of Zirconium-Chrome Azurol S complex

Parameter	Zr-CAS
λ_{max}, (nm)	598
Molar absorptivity, ($L.Mol^{-1}.cm^{-1}$)	3.93×10^3
Sandell's sensitivity (µg/cm^2)	2.54×10^{-4}
Detection Limit (µg/mL)	2.42
Linear Range (µg/mL)	1-7
Stability formation region (pH)	4-5
Acetic acid & Sodium acetate buffer (mL)	1
Chrome Azurol S (0.05%) (mL)	0.3

Table 3 Comparison of two different spectrophotometric techniques for determination of zirconium

S.No	Spectrophotometric techniques (*µg/mL*)	
	Present method	Br-PADAP[39]
1	27.51	26.89
2	18.02	17.76
3	10.15	9.63
4	2.78	2.12
5	11.7	10.10

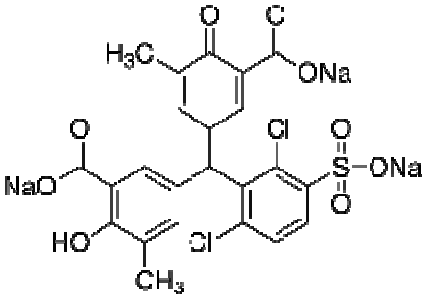

Fig. 1 Structure of Chrome Azurol S

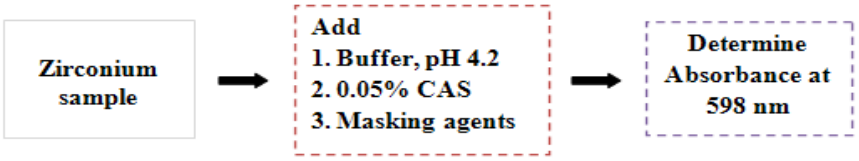

Fig. 2 Reaction for the spectrophotometric detection of zirconium

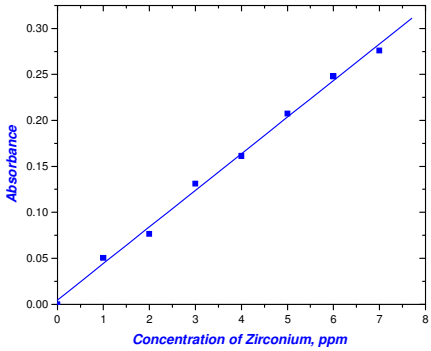

Fig.3 Calibration graph for determination of zirconium at 598 nm

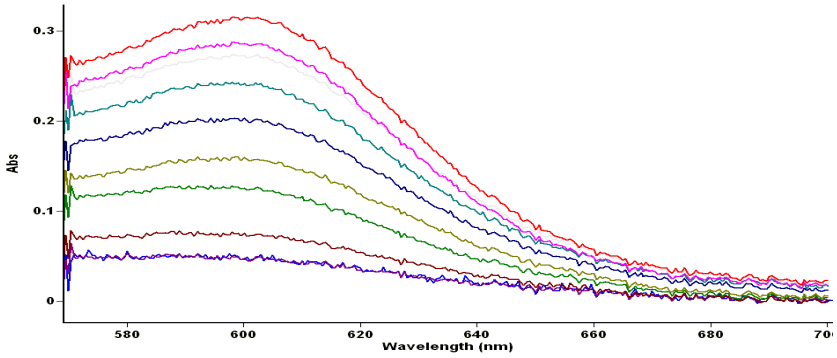

Fig.4 Typical absorption spectrum of zirconium with chrome azurol s at 598 nm

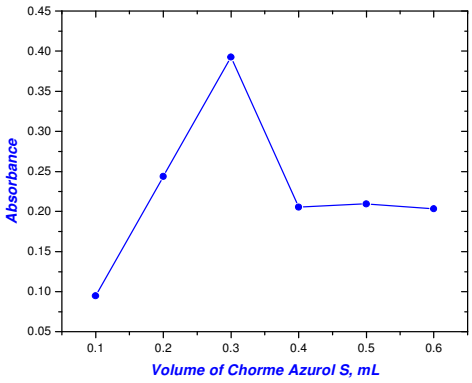

Fig.5 Effect of Chrome Azurol S

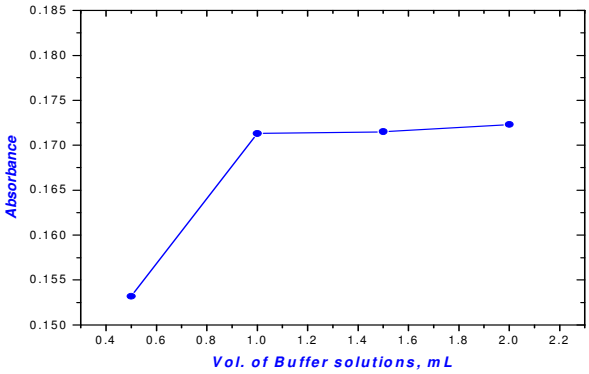

Fig. 6 Effect of Acetate Buffer solutions

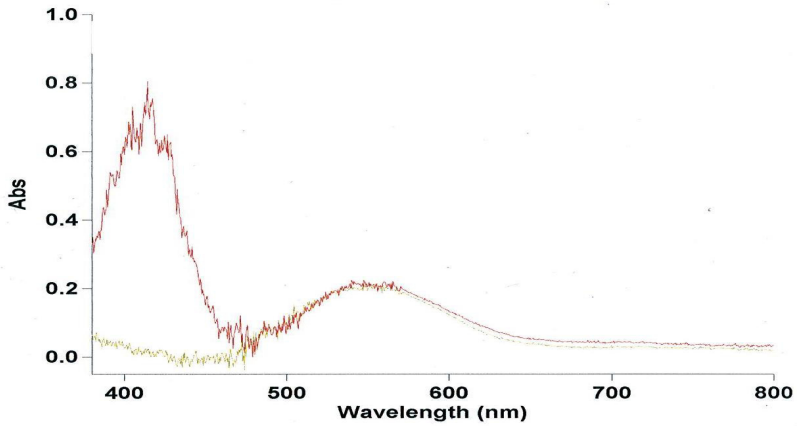

Fig. 7 Typical absorption spectrum of Zr and Uranium

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