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Selective and sensitive spectrophotometric method for the determination of trace amounts of zirconium in environmental and biological samples using 4-chloro-*N*-(2,6-dimethylphenyl)-2-hydroxy-5-sulfamoylbenzamide

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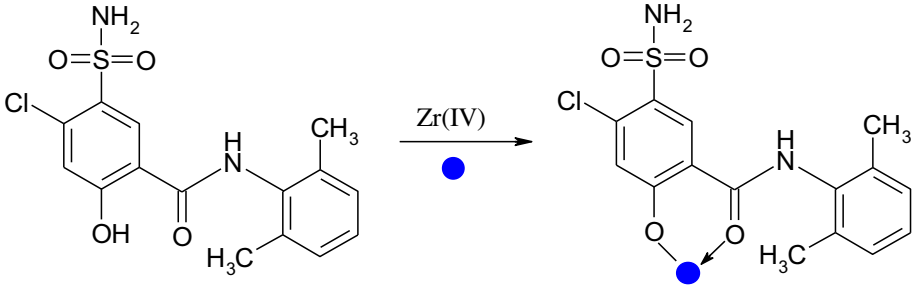
HIGHLIGHTS

- A spectrophotometric method was proposed to determine zirconium in aqueous samples.
- The method was based on the complexation of zirconium and xipamide.
- It is a simple spectrophotometric, very sensitivity and low cost method.
- The important analytical parameters were investigated.
- The method was applied to the determination of Zr(IV) in environmental and biological samples.

GRAPHICAL ABSTRACT

The proposed binding model of Zr(IV) with xipamide.



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ABSTRACT

A simple, selective and sensitive spectrophotometric method for the determination of trace amounts of Zr(IV) in aqueous samples was performed, based on complexation reaction between Zr(IV) and 4-chloro-*N*-(2,6-dimethylphenyl)-2-hydroxy-5-sulfamoylbenzamide (xipamide). The important analytical parameters and their effects on the reported system were investigated. Zr(IV) react with xipamide in the ratio 1:1 in the pH range 8 to form a complex with an absorption maximum 333 nm. The apparent stability constant ($\log\beta_n$) and the free energy change (ΔG^*) of formation of the complex was calculated using the results of mole ratio and continuous variation methods. Beer's law was obeyed in the concentration range 0.2–3.6 μg/mL. For more accurate analysis, Ringbom optimum concentration range was found from 0.3 to 3.5 μg/mL. The molar absorptivity, Sandell sensitivity, detection and quantification limits were also calculated. Taking a constant concentration of Zr(IV) and determining its concentration in the presence of large number of foreign ions tested the effect of foreign ions. The practical applicability of the elaborated method was examined using for determination of mentioned ion in water samples, biological, plant leaves and soil samples where excellent agreements between reported and obtained results were achieved. The relative standard deviation ($n = 6$) were 0.195%. The precision and accuracy of the results were comparable *via F* and *t* test at the 95% confidence level.

Introduction

Zirconium is produced from two ore minerals. The principal economic source of zirconium is the zirconium silicate mineral, zircon ($ZrSiO_4$). The mineral baddeleyite, a natural form of zirconium oxide or zirconia (ZrO_2), is a distant second to zircon in its economic significance. Its hardness and useful properties, such as the ability to increase corrosion resistance and mechanical strength at low and elevated temperature, have made its determination important in special steels and alloys. Also its transparency to thermal neutrons has made it a good construction material in

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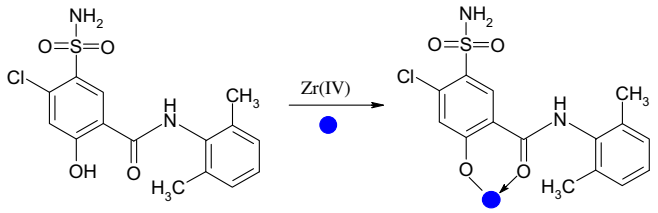

Scheme 1. The proposed binding model of Zr(IV) with xipamide.

nuclear reactors [1]. Zirconium is used as a catalyst in organic reactions, in the manufacture of water repellent textiles, in dye pigments and ceramics, in vacuum tubes, surgical appliances, photoflash bulbs, explosive primers, rayon spinnerets, lamp filaments, etc. [2,3]. As with niobium, zirconium is superconductive at low temperatures and is used to make superconductive magnets, which offer a possibility of realizing direct large-scale generation of electric power [4]. Thus, there is a need for specific and precise determination of zirconium in environmental and biological samples [5].

There are various techniques such as first derivative spectrophotometry [6], potentiometry [7], optical sensor [8], inductively coupled plasma mass spectrometry [9], X-ray fluorescence [10], also one-step procedures such as reversed-phase liquid chromatographic separation [11] or chelating ion exchange followed by spectrophotometric detection [12] have been reported. Also, the determination of zirconium was carried out by energy dispersive X-ray fluorescence after solid phase pre-concentration [13], liquid chromatography separation and determination of its hydroxamic acid chelate [14], and after solid phase extraction [15], also separation using *N*-benzoyl-*N*-phenyl hydroxyl amine supported on a microporous polymeric resin [16], cloud point extraction followed by inductively coupled plasma optical emission spectrometry (ICP-OES) [17], coprecipitation with $Ti(OH)_4$–$Fe(OH)_3$ [18] followed by ICP-OES determination and the spectrophotometric method assisted by chemometric procedures have been proposed [19]. Although these methods have good sensitivity and fast measurement capabilities, they all have some drawbacks, some of which require extensive chemical manipulation and expensive instruments, well-controlled experimental conditions, and complicated sample-pretreatment procedures. Because of the availability of good number of chromogenic reagents with high sensitivities, spectrophotometry is still indispensable method for trace zirconium determinations. The chromogenic reagents commonly used for the determination of zirconium are 3-hydroxy-2-(2′-thienyl)-4H-chromon-4-one [20], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [21], arsenazo-III [22–24], xylenol orange [25], pyrocatechol violet [26], alizarin [27], alizarin red S [28,29], phenyl fluorone [30], bromopyrogallol red [31], morin [32].

This paper describes a simple, selective and sensitive spectrophotometric method for the determination of trace amounts of Zr(IV) in aqueous samples in the presence of some other metal ions. The proposed method was based on the reaction of Zr(IV) with xipamide to form complex which absorb maximally at 333 nm. The proposed method was applied to determine of trace amounts of Zr(IV) in water samples, biological, plant leaves and soil samples. The structure of Zr(IV) with xipamide was given in Scheme 1.

Experimental

Apparatus

UV–vis absorption spectra were measured in 1 cm quartz cells using a Shimadzu UV-1601PC spectrophotometer. The equipment permits multiple expansions in both absorbance and wavelength, and an accuracy of (±0.001) in absorbance readings.

Measurement of pH was performed using a Metrohm-digital model 713 pH meter with a combined glass-calomel electrode of sensitivity (±0.001) pH units. All measurements were performed at room temperature (25 ± 0.01 °C).

Reagents and solutions

All reagents were of analytical grade and double distilled water was used throughout the experiments. Zirconyl chloride octahydrate $ZrOCl_2{\cdot}8H_2O$ was purchased from Merck. The solute xipamide was purchased from Parchem.

Standard stock solutions (1.0×10^{-3} M) of Zr(IV) was prepared by dissolving appropriate amounts of $ZrOCl_2{\cdot}8H_2O$ in water. A stock solution of xipamide reagent of concentration 1.0×10^{-3} M was prepared by dissolving an accurately weighed amount of the reagent in pure methanol. Working solutions were prepared by adequate dilution of the stock solution. Stock solutions of diverse elements were prepared from the high purity salts of cations.

The preparation of universal buffer solution

These buffer solutions were prepared according to Britton [33] involving titration of 100 mL of a mixture of 0.1 M of boric, acetic and phosphoric acid against 0.5 M sodium hydroxide solution to the desired pH covering the range of pH (2.0–12.0) then completing the volume with double distilled water to 250 mL.

Determination of stoichiometry

The experiments for the determination of the stoichiometry of Zr(IV)–xipamide complex was conducted using a UV–vis spectrometry. Job's method of continuous variation [34] was applied to establish the components ratio of the complex. For this, different volumes (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 mL) of 1.0×10^{-5} M Zr(IV) was added with different volumes (2.0, 1.8, 1.6, 1.4, 1.2, 1.0, 0.8, 0.6, 0.4, 0.2, 0 mL) of 1.0×10^{-5} M xipamide and diluted to the volume with double distilled water in 10 mL standard volumetric flask. The absorbance was recorded at λ_{max} of zirconium complex and plotted against the mole fraction of zirconium. Further confirmation of this ratio was ascertained by applying the molar ratio method [35]. For this, different volumes (0.1–2.0 mL) of 1.0×10^{-4} M xipamide was added to constant volume 5 mL of 1.0×10^{-5} M Zr(IV) and diluted to the volume with double distilled water in 10 mL standard volumetric flask. The absorbance was recorded at λ_{max} of the metal complex and plotted against the molar ratio [xipamide]/[Zr(IV)]. The complex stoichiometry was found from the graphs obtained and the conditional stability constant of that complex was calculated using the Harvey and Manning method [36].

Recommended procedure for spectrophotometric determination of Zr(IV)

Into a 10 mL calibrated flask, a suitable aliquot containing between 2 and 36 μg of Zr(IV), 1.8 mL of 1.0×10^{-5} M xipamide solution, and 5 mL universal buffer solution of pH 8.0 were added and completed to the mark with doubly distilled water. The contents of each flask was mixed well at room temperature (25 ± 5 °C) and the absorbance was measured at 333 nm against the reagent blank prepared similarly in 10 mm reference cell within the stability time period of 24 h. The concentration of zirconium was calculated either from a calibration curve or regression equation.