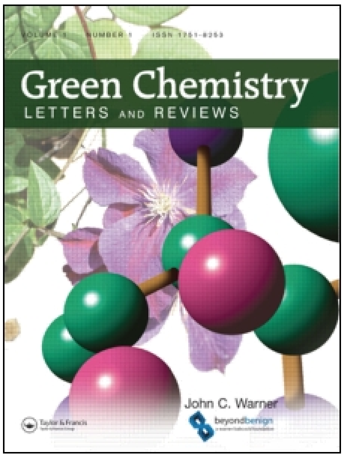

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ORIGINAL ARTICLE

Application of acidic extract of *Platanus orientalis* tree leaves as a green reagent for selective spectrophotometric determination of zirconium

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A novel spectrophotometric method for the determination of zirconium by using a new reagent, acidic extract of *Platanus orientalis* tree leaves is developed. In 6 M hydrochloric acid, zirconium reacts with this reagent to form a yellow product. The formed product shows maximum absorbance at 422 nm with a molar absorptivity value of $0.59 \times 10^{-}$ l mol^{-1} cm^{-1} and the method was linear in the 0.4–8 µg mL^{-1} concentration range. The detection limit value was found to be 0.086 µg mL^{-1}. The proposed method was simple, clean, low cost, selective, and sensitive. It was applied to the determination of zirconium in tap water, wastewater and well water samples with relative standard error of less than 2.5%.

Keywords: *Platanus orientalis* tree leaves; zirconium; spectrophotometric determination

Introduction

Zirconium is one of the abundant elements and is widely distributed in the Earth's crust. Most of the zirconium is used as compounds for the ceramic industry, refractories, glazes, enamels, foundry mold and abrasive grits and compounds for electrical ceramics. The incorporation of zirconium oxide in glass significantly increases its resistance to alkali. Zirconium metal is used almost entirely for cladding uranium fuel elements for nuclear power plants. Another significant use is in photoflash bulbs. Some chemical processing industries use zirconium metal for corrosion-resistant vessels and piping, particularly for withstanding hydrochloric (HCl) and sulfuric acids (*1*,*2*).

The direct determination of Zr^{4+} ion in alloys and other samples is of great importance from an analytical point of view. There are numerous methods outlined for the spectrophotometric determination of Zr^{4+} ion in literature (*3–13*). However, some of these methods have both low sensitivity and low selectivity (*10*,*12*) while others have high sensitivity but low selectivity in the presence of some ions or molecules (*2–6*). Arsenazo III (*3–10*), alizarin S (*10*,*11*), pyrocatechol violet (*10*), xylenol orange (*10*,*12*), 2,4-dinitrophenol-(6-azo-1)-2-naphtol-3,6-disulfonic acid (Picramine P) (*7*,*8*) and 2,4-dinitrophenol-(6-azo-2)-1-naphtol-3,8-disulfonic acid (Picramine ε) (*9*) have all been proposed to be good ligands for the spectrophotometric determination of Zr^{4+}. However, the determination of Zr^{4+} ion with alizarin S, pyrocatechol violet, and xylenol orange cannot be carried out until after separating interfering species (*7*,*11*,*12*). The determination of Zr^{4+} with arsenazo III is generally carried out in 0.1–3 M HCl media. The presence of F^{-}, SO_4^{2-}, PO_4^{3-}, organic hydroxy acids, Hf^{4+}, Th^{4+}, and U^{6+} in these media interferes the reaction of arsenazo III reagent with Zr^{4+} (*3*,*7*). The reactions of Picramine P and Picramine ε with Zr^{4+} give color compounds in 1 M HCl. The determination is interfered by the ions, such as Fe^{3+}, Cr^{3+}, Cu^{2+}, Be^{2+}, Si^{4+}, Sn^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, W^{6+}, Hf^{4+}, Hg^{2+}, and Re^{4+}. Thus, one of the most important problems in using these reagents for the determination of zirconium is the need for separating the interfering ions from the medium that causes time-consuming pretreatment steps (*8*,*9*).

Despite the usefulness and importance of synthetic reagents in the determination of metal ions, most of these reagents are highly toxic and undoubtedly have a detrimental impact on the human health and environment. Furthermore, organic solvents that are used as a main agent to synthesize these reagents are more dangerous than their products. Some intrinsic characteristics of most organic solvents are their high flammability, volatility, and toxicity. During the last decade, intensive researches have been done toward environmentally benign substitutes for

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volatile and toxic organic solvents and finding the techniques that reduce usage and exposure of these materials (*14–16*).

The native range of the *Platanus orientalis* includes at southern Eurasia from west central Italy, southeast Europe, especially in London and at least Eurasia from the Balkans to Iran. It is often called *Platanus* or related names in Europe, and *Chenar* or related names from Turkey to India. It is often found naturally in riverine settings, together with such trees as alder, willow, and poplar. However, it is quite capable of survival and success in dry soils once it is established. Like other Plane trees, its leaves are borne alternately on the stem, deeply lobed, and palmate or maple-like (Figure 1). The leaves and bark have been used medicinally (astringent, ophthalmic, and vulnerary). A fabric dye has been made from the twigs and roots. The timber, often called lacewood, is figured and valuable for indoor furniture (*17–21*).

In this paper, we introduce a clean and novel procedure for spectrophotometric determination of zirconium(IV) in water samples. The method is based on the color reaction of Zr^{4+} with a new chromogenic reagent, acidic extract of *Platanus orientalis* tree leaves. As the determination was carried out directly in aqueous solution, the method has advantages such as simplicity, selectivity, and sensitivity and has been successfully applied to determine Zr^{4+} in real samples. A comparison of the analytical features of the developed method with those of previously reported methods for spectrophotometric determination of zirconium is given in Table 1. In addition, in this study two natural substances were used to prepare acidic extract, tree leaves, and water. Against organic solvents and synthetic reagents that are very hazardous for human health and environment, water and tree leaves can surely be expressed in terms of environmental impact, safety, costs, and availability.

Experimental section

Reagents and chemicals

All reagents used were of analytical reagent grade and the solution was prepared with distilled water unless otherwise specified. A stock Zr^{4+} solution was prepared by dissolving appropriate amounts of $ZrOCl_2 \cdot 8H_2O$ (Merk) in 100 mL of 0.1 M HCl to make a 1000 μg mL^{-1} solution. A 100 μg mL^{-1} working standard solution was prepared by accurate dilution of the stock solution with water. Stock solutions of diverse ions were prepared from the high purity compounds (99.99%, Merck).

Apparatus

A Cary-3 UV–visible spectrophotometer with 10 mm quartz cells was used to record absorption spectra and measure absorbance.

Preparation of reagent solution

The optimum conditions for the preparation of a stable reagent solution have been achieved as follows: The local *Platanus orientalis* tree leaves were washed and dried in an oven at 60°C for a period of 24 h, and then ground and sieved to obtain uniform material (100 μm). Two grams of sieved leaves was contacted with 50 mL of 0.1 M HCl (10 h) and the solution was filtered with filter paper. Finally, the filtrate solution was contacted with 1 M HCl (20 h) then filtered and used as reagent solution. The contact with HCl causes stability and reproducibility of product absorbance. This reagent is stable for about 48 h in the normal temperature (25°C) and at least 10 days if it is maintained in the temperature of 5°C.

Experimental procedure

A solution containing no more than 40 μg of zirconium was transferred into a 5 mL calibrated

Figure 1. *Platanus orientalis* tree and its leaf.

Table 1. Comparison of characteristic features of various spectrophotometric methods for the determination of zirconium.

Reagent	Optimum pH or acidity	γ_{max} (nm)	Molar absorption coefficient	Remarks	References
Arsenazo III	HCl, 1 M	680	12,500	Th^{4+}, U^{6+}, Hf^{4+}, Ce^{3+} interfere	(*3–10*)
Arsenazo I	1.5	580	9700	Poor sensitivity, many metals interfere	(*10, 11*)
Alizarin S	1.8	540	6500	Many metals interfere	(*10, 11*)
Xylenol orange	1.5	560	52,000	Many metals interfere	(*10, 12*)
Pyrocatechol violet	5	600	31,000	Many metals interfere	(10)
Picramine P	HCl, 1.2 M	565	23,000	Many metals interfere	(*7, 8*)
Thoron	2	570	3200	Poor sensitivity, many metals interfere	(*10, 11*)
Acidic extract of *Platanus orientalis* tree leaves	HCl, 6 M	422	5900	Sensitive and selective	Present method

flask. Subsequently, 2.5 mL of concentrated HCl and 2 mL of reagent solution were added. The volume was made up to the mark with distilled water and the solution was mixed. After 30 min, the absorbance was measured at 422 nm against a reagent blank in a 10 mm cell.

Procedure for interference studies

Under the optimum conditions, the effects of various foreign ions on the determination of Zr^{4+} were studied separately according to the procedure described above. An aliquot containing an amount of zirconium within the range recommended for the method was transferred into a 5 mL volumetric flask, 2 mL of complexing agent solution was added after addition of 2.5 mL concentrated HCl. Then different amounts of diverse ions were added to the above mixture. The tolerance limit of an ion was taken as the maximum amount causing an error not greater than 5%.

Procedure for water samples

Tap water, well water, and wastewater samples were filtrated and collected in polyethylene bottles. HCl (1:1) was added to neutralize the alkalinity. Then the determination method given above was applied for a known volume of the sample.

Results and discussion

Absorption spectra

There are many compounds in acidic extract of *Platanus orientalis* tree leaves, such as plastids, proteins, and pigments. The color of a leaf depends on the amount and types of pigments that are present. Chemical interactions within the plant, particularly in response to acidity (pH) also affect the leaf color. The main pigment classes responsible for leaf color are porphyrins, carotenoids, and flavonoids (*22*). Each pigment has a specific color. It is supposed that one of these pigments is responsible for the chromogenic reagent. For example, chlorophyll is a chelating agent that has a porphyrin ring in its structure and can easily combine with metal ions (*23*). However, it is mentioned that there has not been any work on reagent structure in this study.

In HCl medium, Zr^{4+} reacts with reagent to form a yellow product. The absorption spectra of the Zr^{4+} in the reagent solution, along with its reagent blank, are shown in Figure 2. All the spectral curves were recorded for solutions in 6 M HCl. It can be seen that the product has an absorption peak at 422 nm that may be used for the direct determination of zirconium(IV) in aqueous media.

Optimization of the reaction medium

In the preliminary experiments, the effect of chemical medium on the reaction between Zr^{4+} and reagent was studied. For this purpose, absorption spectra of the Zr^{4+} in the range of 250–780 nm, in the different concentrations of various acids and also different pH

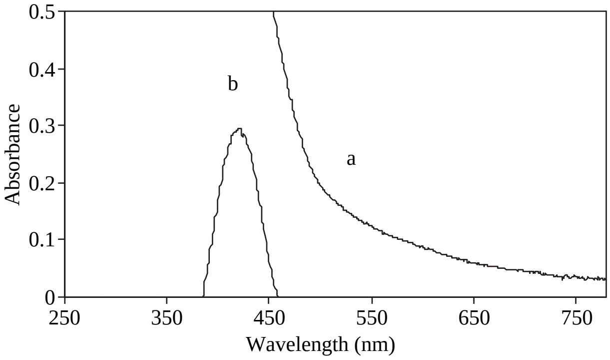

Figure 2. Absorption spectra of: (a) reagent solution vs. water blank; (b) product vs. reagent blank. [Zr^{4+}], 5 μg mL^{-1}; volume of reagent, 2 mL; HCl concentration, 6 M.

Table 2. Effect of the reaction medium on the absorbance.

Reaction medium	Maximum absorbance in the range of 250–780 nm
pH 6	0.010
pH 3	0.018
HNO_3 (1 M)	0.008
HNO_3 (5 M)	–
H_2SO_4 (1 M)	–
H_2SO_4 (5 M)	–
$HClO_4$ (1 M)	0.009
$HClO_4$ (5 M)	–
HCl (1 M)	0.041
HCl (5 M)	0.212

Note: Conditions: [Zr^{4+}], 5 μg mL^{-1}; volume of reagent, 1.5 mL.

values (adjusted by HCl and sodium hydroxide) were examined. The results are summarized in Table 2. As is seen, a significant absorbance can be seen only in high concentration of HCl and HCl is the most suitable medium for the reaction between reagent and Zr^{4+}.

Effect of hydrochloric acid (HCl) concentration

The effect of HCl concentration on the determination of zirconium(IV) was investigated spectrophotometrically. The results obtained are shown in Figure 3. As it is clearly seen, the sensitivity was the highest at 6 M HCl. Therefore, a concentration of 6 M HCl was chosen in the determination procedure.

Effect of the volume of reagent solution

The influence of the volume of chromogenic agent (0.5–2.5 mL) on the absorbance was studied, at the optimum reaction acidity, by measuring the absorbance of 5 mL of a solution containing 25 μg Zr^{4+} and various amounts of reagent solution at 422 nm. The results are shown in Figure 4. Maximum and constant absorbance was obtained over the volume range of 2–2.5 mL of reagent solution. In the procedures, 2.0 mL of reagent solution was utilized.

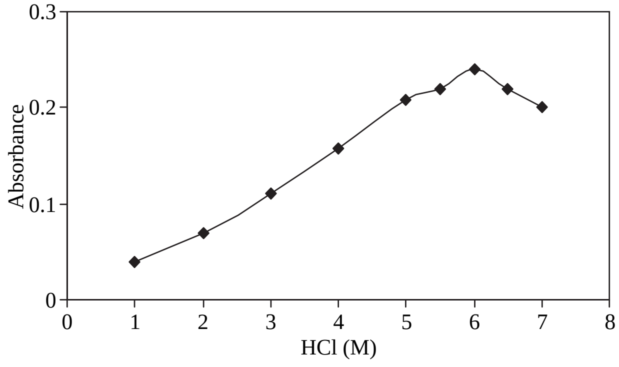

Figure 3. Effect of HCl concentration. [Zr^{4+}], 5 μg mL^{-1}; volume of reagent, 1.5 mL.

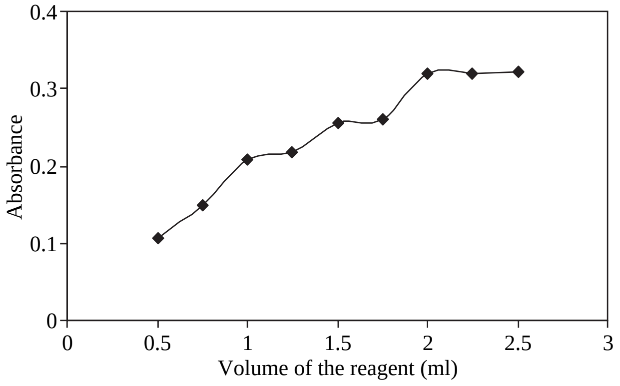

Figure 4. Effect of reagent volume. [Zr^{4+}], 5 μg mL^{-1}; HCl concentration, 6 M.

Rate of reaction and stability of the system

The reaction between Zr^{4+} and reagent was completed at room temperature. Maximum and constant absorbance at 422 nm was observed within 30 min, and remains constant for at least 10 h. Therefore, a standing time of 30 min was selected for the measurements.

Calibration curve and sensitivity

The calibration curve for the determination of zirconium(IV) was obtained under the optimum conditions. The Beer's law was obeyed over the range 0.4–8 μg mL^{-1} Zr^{4+} concentration (Figure 5). The linear regression equation was: $A = 0.057 + 0.053C_{Zr}$ (μg mL^{-1}). The correlation coefficient was 0.997. The apparent molar absorption coefficient (ε) calculated from the slope of calibration curve was 0.59×10^4 l mol^{-1} cm^{-1}. The limit of detection (LOD) achieved for Zr^{4+}, estimated by $3S_b/m$ (where S_b is the standard deviation of 10 measurements of the blank and m is the slope of the calibration line), was

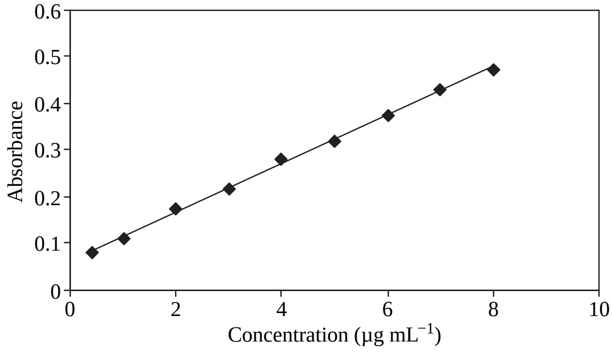

Figure 5. Analytical curve for the determination of zirconium.

Table 3. Tolerated ratio of various foreign ions.

Ion	Tolerance ratio	Ion	Tolerance ratio
Na^{+}	1000	La^{3+}	1000
K^{+}	1000	Ce^{3+}	1000
Ca^{2+}	1000	UO_2^{2+}	1000
Mg^{2+}	1000	Th^{4+}	1000
Ba^{2+}	1000	Ti^{4+}	1000
Ni^{2+}	1000	Fe^{3+}	2
Mn^{2+}	1000	Hf^{4+}	2
Co^{2+}	1000	NO_3^{-}	1000
Zn^{2+}	1000	I^{-}	1000
Cd^{2+}	1000	SCN^{-}	200
Pb^{2+}	1000	CH_3COO^{-}	200
Hg^{2+}	1000	SO_4^{2-}	100
Ag^{+}	1000	EDTA	100
Pd^{2+}	1000	$C_2O_4^{2-}$	40

0.086 μg mL^{-1} for the analyte. The relative standard deviation was 2.5% under 10 determinations for 5 μg mL^{-1} of Zr^{4+}.

Interference studies

The effect of various cations and anions on the determination of zirconium(IV) was investigated (Table 3). The tolerance limit was taken as the amount that caused ±5% absorbance error in the determination of 2 μg mL^{-1} of Zr^{4+}. The results indicate that most of the cations did not show any significant spectral interference at concentrations 1000 times greater that those of the analytes. Although Hf^{4+} and Fe^{3+} could cause some problems, these cations could be tolerated at concentrations two times greater than Zr^{4+}.

Table 4. Determination of zirconium in the water samples by the proposed method.

Sample	Zirconium added (μg mL^{-1})	Zirconium found (μg mL^{-1})	Recovery (%)
Tap water	0.50	0.53 (1.9)*	106
	3.00	2.95 (1.2)	98.3
	5.00	4.95 (1.7)	99
Well water	0.50	0.47 (2.1)	94
	3.00	3.05 (1.3)	101.6
	5.00	4.88 (0.9)	97.6
Wastewater	0.50	0.52 (1.7)	104
	3.00	2.88 (1.9)	96
	5.00	4.83 (2.3)	96.6

*Values in parentheses are RSDs based on three replicate analyses.

Table 5. Determination of zirconium in the wastewater samples by the proposed and Arsenazo III methods.

	Zirconium found (μg mL^{-1})	
Sample	Proposed method	Arsenazo III
Wastewater 1	11.24 (2.4)*	11.65 (1.6)
Wastewater 2	12.96 (1.9)	13.24 (2.1)

*Values in parentheses are RSDs based on three replicate analyses.

Analytical application

The proposed method was applied successfully to the determination of zirconium ion in tap water, well water, and wastewater samples. The results are shown in Table 4. The recoveries are close to 100% and indicate that the proposed method was helpful for the determination of zirconium in the real samples. In addition, this method was applied to the determination of zirconium in two wastewater samples (ceramic industry). The results are given in Table 5. As seen, there is good agreement between the results obtained by the proposed method and the arsenazo III method. It proved that the method can be used for zirconium determination in water samples.

Conclusions

A new reagent, acidic extract of *Platanus orientalis* tree leaves, for the determination of Zr^{4+} ion has been developed. This reagent showed the maximum sensitivity for Zr^{4+} in 6 M HCl. The determination of Zr^{4+} with this reagent has certain advantages compared with the other known methods in literature: First, this is a new reagent for the determination of Zr^{4+} that can be easily prepared without any cost. Second, it is much more sensitive and selective compared with the other methods that need the time-consuming separation or pretreatment steps. Finally from an environmental point of view, this study uses natural substances as main components to prepare the reagent and does not employ any hazardous materials consisting of organic solvents. Therefore, the proposed method is a green and reliable technique for the determination of zirconium in aqueous solutions.

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