A Comparison between Reagents Extracted from Tree Leaves for Spectrophotometric Determination of Hafnium(IV)

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Abstract—The main goal of this paper was to make use of green reagents as a substitute of perilous synthetic reagents and organic solvents for spectrophotometric determination of hafnium(IV). The extracts taken from six different kinds of tree leaves including *Acer negundo, Ficus carica, Cerasus avium, Chimonanthus, Salix babylonica* and *Pinus brutia*, were applied as green reagents for the experiments. In 6-M hydrochloric acid, hafnium reacted with the reagent to form a yellow product and showed maximum absorbance at 421 nm. Among tree leaves, *Chimonanthus* showed satisfactory results with a molar absorptivity value of 0.61×10^4 l mol^{-1} cm^{-1} and the method was linear in the 0.3-9 µg mL^{-1} concentration range. The detection limit value was 0.064 µg mL^{-1}. The proposed method was simple, low cost, clean, and selective.

Keywords—Spectrophotometric determination, tree leaves, synthetic reagents, hafnium.

I. Introduction

EVERY year to spectrophotometrically assay hafnium ions, many synthetic reagents such as Arsenazo III [1], alizarin S [2], methylthymol blue [3], etc. are synthesized, used and finally wasted in the nature. 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. These reagents include a broad spectrum of different chemical structure, primarily based on substituted aromatic and heterocyclic groups such as aromatic amine, phenyl and naphthyl which represent a potentially important class of organic pollutants. The degradation of synthetic organic analytical reagents in the environment by microorganism is likely to be slow due to their structures, which means that it is possible for high levels of them to persist and potentially accumulate [4]. Furthermore, any degradation that does occur may produce smaller molecules equally unfamiliar to environment, such as amine may also be hazardous. Moreover, some no-degradable compounds discharged into the environment can cause serious problems because they usually come back to human through the several channels such as bioaccumulation [5]. 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,

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intensive researches have been done toward environmentally benign substitutes for volatile and toxic organic solvents and finding the techniques that reduce usage and exposure of these materials [6], [7].

Reagents based on biomaterial are inherently nontoxic, low cost, biodegradables, locally available and renewable resources which promote the principles by expanding opportunities which may produce a significant amount of manufacturing, pharmaceutical and consumer materials which are currently produced with nonrenewable and sometimes hazardous materials. Nowadays, some of the tree leaves are traditionally consumed as beverages, food flavorings and even as invaluable medicinal herbs by the folks to treat diabetes, dizziness, high blood pressure, and neuralgia [8]-[10]. In this study, another application of tree leaves has been introduced. The purposed method is based on the color reaction of Hf(IV) with a green chromomeric reagent, acidic extract of tree leaves for determination of hafnium(IV).

II. Materials and Methods

A. Apparatus

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

B. Reagents and Chemicals

All reagents used were of analytical grade and the solutions were prepared with distilled water unless otherwise specified. A stock Hf(IV) solution was prepared by dissolving appropriate amounts of HfOCl$_2$·8H$_2$O (Merck) 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 distilled water.

C. Preparation of Reagent Solution

The reagent solutions for determination of hafnium(IV) has been prepared as follows. Six different kinds of local tree leaves (Fig. 1) 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 m). A quantity of 2 g of each of the sieved leaves was contacted with 50 ml of 0.1 M HCl (10 h), and the solutions were filtered with filter paper. Finally, the filtrate solutions were contacted with 1 M HCl (40 h) then filtered and used as reagent solutions (acidic extract) for determination of hafnium(IV). 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.
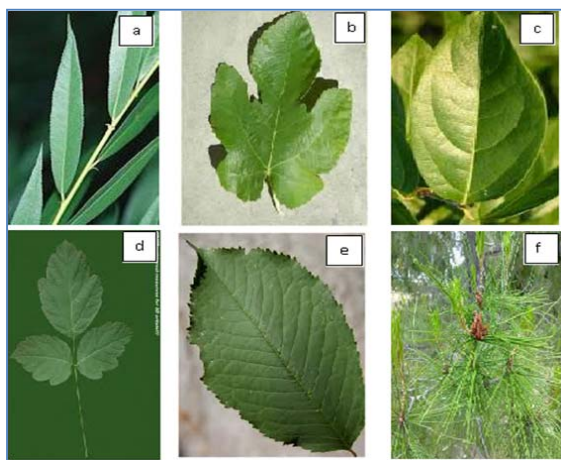

Fig. 1 Six different kinds of local tree leaves: (a) *Salix babylonica*; (b) *Ficus carica*; (c) *Chimonanthus*; (d) *Acer negundo*; (e) *Cerasus avium*; (f) *Pinus brutia*

D. Experimental Procedure

Experimental Procedures for determination of hafnium(IV) was performed as follows. For determination of hafnium(IV), a known concentration of hafnium(IV) was transferred into a 5-ml calibrated 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 90 min, the absorbance was measured at 421 nm against a reagent blank in a 10-mm cell.

III. RESULTS AND DISCUSSIONS

A. Selection the Tree Leaf for Spectrophotometric Determination of Hafnium

There are many compounds in acidic and water extract of 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, 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 [11]. However, it is mentioned that there has not been any work on reagent structure in this study. In the preliminary experiments it was found that except *Salix babylonica* and *Pinus brutia*, acidic extract of other tree leaves can easily be applied for assaying of metal ions. As shown in Table I, among tree leaves *Chimonanthus* showed satisfactory results and thus its reagent was used in the next experiments.

B. Absorption Spectra

In hydrochloric acid medium, Hf(IV) reacts with Chimonanthus reagent to form a yellow product. The absorption spectra of the Hf(IV) in the reagent solution, along with its reagent blank, are shown in Fig. 2. All the spectral curves were recorded for solutions in 6 M hydrochloric acid. It can be seen that the product has an absorption peak at 421 nm that may be used for the direct determination of hafnium(IV) in aqueous media.

TABLE I
SOME TREE LEAVES FOR SPECTROPHOTOMETRIC DETERMINATION OF HAFNIUM (IV)

Leaf type	L.R	ε	R^2	RSD
1- *Acer negundo*	2-7	2589	0.993	2.1
2- *Ficus carica*	2-11	2615	0.998	2.3
3- *Cerasus avium*	1-7	2977	0.997	1.8
4- *Salix babylonica*	-	-	-	-
5- *Chimonanthus*	0.3-9	6079	0.997	2.2
6- *Pinus brutia*	-	-	-	-

L.R: Linear range (µg/ml), ε: The apparent molar absorption coefficient (l mol^{-1} cm^{-1}), R^2: The correlation coefficient, RSD: The relative standard deviation for ten determinations for 4 µg ml^{-1} of Zr (IV).
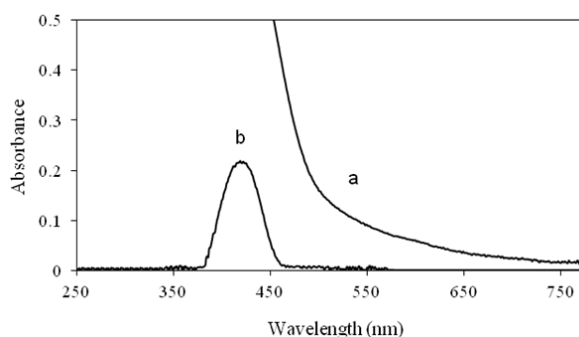

Fig. 2 Absorption spectra of (a) Reagent solution vs. water blank, (b) Product vs. reagent blank. [Hafnium]: 8 µg ml^{-1}, Volume of reagent: 2 ml, HCl concentration: 6 M

C. Effect of Hydrochloric Acid Concentration

The effect of different acids on the absorbance of product species had been investigated using HCl, HNO_3, H_2SO_4 and CH_3COOH. These colored species are unstable in nitric acid and sulphuric acid and do not give maximum color intensity in acetic acid medium. It was found that hydrochloric acid is most suitable media for reaction between reagent and Hf(IV). The effect of hydrochloric acid concentration on the determination of hafnium(IV) was investigated spectrophotometrically. The results obtained are shown in Fig. 3. As it is clearly seen, the sensitivity was the highest at 6 M hydrochloric acid. Therefore, a concentration of 6 M hydrochloric acid was chosen in the determination procedure.

D. Effect of the Volume of Reagent Solution, Rate of Reaction and Stability of the System

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 50 µg Hf(IV) and various amounts of reagent solution at 421 nm. The results are shown in Fig. 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. The reaction between Hf(IV)

with reagent was completed at room temperature. Maximum and constant absorbance at 421 nm was observed within 30 min and remained constant for at least 10 h. Therefore, a standing time of 30 min was selected for the measurements.
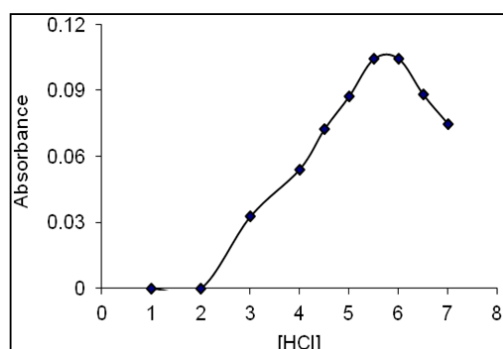

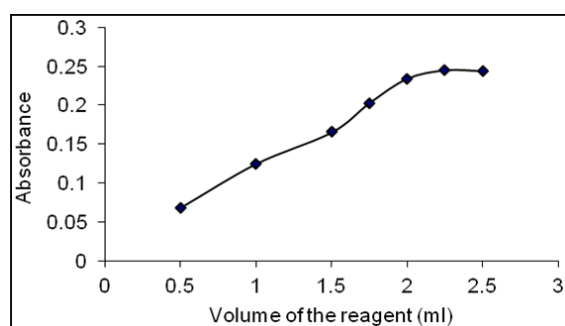Fig. 3 Effect of HCl concentration. [Hf(IV)]: 8 µg ml^{-1}, Volume of reagent: 1 ml

Fig. 4 Effect of reagent volume. [Hf(IV)]: 8 µg ml^{-1}, HCl concentration: 6 M

E. Calibration Curve and Sensitivity

The calibration curve for determination of hafnium(IV) was obtained under the optimum conditions. The Beer's law was obeyed over the range 0.3–9 µg ml^{-1} Hf(IV) concentration. The linear regression equation was: $A = 0.0035 + 0.0633C_{Hf}$ (µg ml^{-1}). The correlation coefficient was 0.997. The apparent molar absorption coefficient (ε) was 0.61×10^4 l mol^{-1} cm^{-1} calculated from the slope of calibration curve. The limit of detection (LOD) achieved for Hf(IV), 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 0.064 µg ml^{-1} for the analyte. The relative standard deviation was 2.2 % under ten determinations for 10 µg ml^{-1} of Hf(IV).

F. Interference Studies

The effect of various cations and anions on the determination of hafnium(IV) was investigated (Table II). The tolerance limit was taken as the amount that caused ±5% absorbance error in the determination of 5 µg ml^{-1} of Hf(IV). The results indicate that most of the cations did not show any significant spectral interference at concentrations 400-times greater than those of the analytes; although Zr^{4+} and Fe^{3+} could cause some problems in high concentrations.

G. Analytical Application

The studied procedure can be successfully used for the determination of Hf(IV) in various aquatic matrix. The results are shown in Table III. The recoveries are close to 100% and indicate that the proposed method is helpful for the determination of hafnium(IV) in the real samples.

TABLE II
TOLERATED LIMIT OF VARIOUS FOREIGN IONS

Ion	Tolerance limit (µg ml^{-1})	Ion	Tolerance limit (µg ml^{-1})
La^{3+}	1500	Li^+	2000
Ce^{3+}	1500	Na^+	2000
UO_2^{2+}	1000	K^+	2000
Th^{4+}	1000	Ca^{2+}	2000
Ti^{4+}	1000	Mg^{2+}	2000
Fe^{3+}	2	Ba^{2+}	2000
Zr^{4+}	0.4	Ni^{2+}	2000
NO_3^-	1000	Co^{2+}	2000
I^-	1500	Zn^{2+}	2000
SCN^-	1000	Cd^{2+}	2000
CH_3COO^-	1000	Pb^{2+}	2000
SO_4^{2-}	500	Hg^{2+}	2000
EDTA	500	Ag^+	2000
$C_2O_4^{2-}$	200	Pd^{2+}	2000

TABLE III
DETERMINATION OF HAFNIUM(IV) IN THE WATER SAMPLES BY THE PROPOSED METHOD

Sample	Hafnium(IV) added (µg ml^{-1})	Hafnium(IV) found (µg ml^{-1})	Recovery (%)
Tab water	1.00	0.98 (1.6)[a]	98
	5.00	4.93 (0.7)	98.6
	10.00	10.04 (1.7)	100.4
Well water	1.00	1.01 (0.9)	101
	5.00	5.06 (2.1)	101.2
	10.00	9.91 (1.6)	99.1
Waste water	1.00	0.97 (1.7)	98
	5.00	4.97 (1.8)	99.4
	10.00	9.85 (2.2)	98.5

[a]Values in parentheses are R.S.D.s based on three replicate analyses.

IV. CONCLUSION

As mentioned in experimental section, two eco-friendly substances were used to prepare acidic extracts, 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. Finally, the proposed method can easily and safely be used for spectrophotometric determination of studied metal ions in all over the world.

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