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A Green Method for Selective Spectrophotometric Determination of Hafnium(IV) with Aqueous Extract of *Ficus carica* Tree Leaves

A. Boveiri Monji, H. Yousefnia, M. Haji Hosseini, S. Zolghadri

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***Abstract*—**A clean spectrophotometric method for the determination of hafnium by using a green reagent, acidic extract of *Ficus carica* tree leaves is developed. In 6-M hydrochloric acid, hafnium reacts with this reagent to form a yellow product. The formed product shows maximum absorbance at 421 nm with a molar absorptivity value of 0.28×104 l mol^{-1} cm^{-1}, and the method was linear in the 2-11 μg ml^{-1} concentration range. The detection limit value was found to be 0.312 μg ml^{-1}. Except zirconium and iron, the selectivity was good, and most of the ions did not show any significant spectral interference at concentrations up to several hundred times. The proposed method was green, simple, low cost, and selective.

***Keywords*—**Spectrophotometric determination, *Ficus carica* tree leaves, synthetic reagents, hafnium.

I. Introduction

THE group 4 lying in the d-block of the periodic table contains elements of titanium (Ti), zirconium (Zr), hafnium (Hf) and rutherfordium (Rf). Hf chemically resembles Zr and is found in many Zr minerals [1]. Hf-based compounds are employed in gate insulators in the 45 nm generation of integrated circuits from Intel, IBM and others. Hf oxide-based compounds are practical high-k dielectrics, allowing reduction of the gate leakage current which improves performance at such scales [2]-[4]. Hf is used for alloying with iron, Ti, aluminium and other metals. Because Hf absorbs neutrons better than any other metal and is resistant to corrosion, it is applied to control nuclear reactions. Hf is resistant to corrosion due to the presence of hard and impenetrable oxide layer on its surface. Also, it has a very high melting point thus is applied in high-temperature ceramics and alloys [5], [6].

The direct determination of Hf ions in alloys and other samples is of great importance in analytical point of view. The development of a highly sensitive and selective spectrophotometric method for Hf(IV) is essential. The use of electrothermal atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry improve sensitivity but these methods are time-consuming and generally involve expensive instrumentation which is not available at all laboratories [7].

A. Boveiri Monji, H. Yousefnia, M. Haji Hosseini and S. Zolghadri are with the Material and Nuclear Fuel Research School, Nuclear Science and Technology Research Institute (NSTRI), Tehran, Iran (e-mail: abovairi@aeoi.org.ir, hyousefnia@aeoi.org.ir, majid2_haji@yahoo.com, s_zolghadri63@yahoo.com).

At present, one of the most common methods for the determination of metal ions is the spectrophotometric methods. Several chromogenic reagents have been utilized in spectrophotometric determinations of hafnium [8]-[14]. however, the number of reagents available for the spectrophotometric determination of Hf is relatively low.

Arsenazo III [15], [16], alizarin S [17], xylenol orange [18], [18], methylthymol blue [18], 1-(2-pyridylazo)-2-naphthalenol (PAN) [19], and with 4-(2-thiazolylazo)resorcinol (PAR) [20], were reported earlier for spectrophotometric determination of Hf(IV). These reagents have its own advantages and disadvantages. The determination is interfered by the ions such as Cr^{3+}, Cu^{2+}, Fe^{3+}, Be^{2+}, Si^{4+}, Sn^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+}, Cd^{2+}, Zr^{4+}, W^{6+}, Hg^{2+}, Re^{4+} and so on. These methods have the disadvantage of the need of separating the interfering ions from the medium before Hf can be determined [21].

Ficus carica is an Asian species of flowering plant in the mulberry family, known as the common fig (Fig. 1). Figure is planted throughout the Mediterranean region and is well adapted to drought and high temperatures. This plant is widely grown for its fruit and is commercially grown in the United States in Texas, California, Oregon, and Washington. The tree with small size of 3-9 m (10 to 30 ft) high, many spreading branches, and a trunk rarely exceeds over 7 (17.5 cm) in diameter originally belongs to the western Asia and Middle East. Although it has been planted for a long time, it is now rampantly grown around the world [15]-[17].

Reagents based on biomaterial are inherently nontoxic, low cost, biodegradable, 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 [25]-[27]. 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 new chromogenic reagent, acidic extract of *Ficus carica* tree leaves. In addition to the sensitivity, simplicity, selectivity and low cost, this green reagent can be used directly in aqueous solution for determination of Hf without the use of organic solvents.

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Fig. 1 Tree leaves of *Ficus carica*

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

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 $HfOCl_2 \cdot 8H_2O$ (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 Solutions

The stable reagent solution was obtained according to the following steps. To obtain a leaf of 100-µm particle size, the local *Ficus carica* tree leaves were first washed with distilled water and then dried in an oven at 70 °C for 7 hours. 2 g of sieved tree leaf was contacted with 50 ml of 0.1 M hydrochloric acid for 20 hours and the solution was filtered with filter paper. Finally, the obtained filtered liquid was contacted with 1 M hydrochloric acid for 40 hours then filtered and applied as chromogenic reagent for determination of Hf.

D. Experimental Procedure

2.5 ml of concentrated hydrochloric acid solution is put into a 5-ml calibrated flask, then appropriate volume of Hf(IV) solution and 2 ml of reagent solution are added. The volume is made up to the mark with distilled water, and the solution is mixed. After 90 min, the absorbance is measured at 421 nm against a reagent blank in a 10 mm cell.

III. Results and Discussions

A. Absorption Spectra

In hydrochloric acid medium, Hf(IV) reacts with 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 Hf(IV) in aqueous media

B. 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 the most suitable media for reaction between reagent and Hf(IV). The effect of hydrochloric acid concentration on the determination of Hf(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.

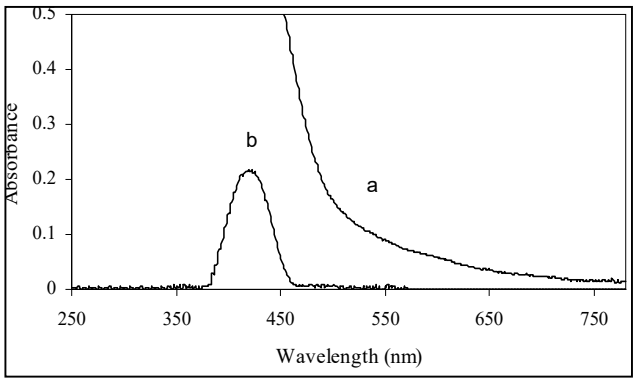


Fig. 2 Absorption spectra of (a) Reagent solution vs. water blank, (b) Product vs. reagent blank. [Hf(IV)]: 5 µg ml^{-1}, Volume of reagent: 2 ml, HCl concentration: 6 M

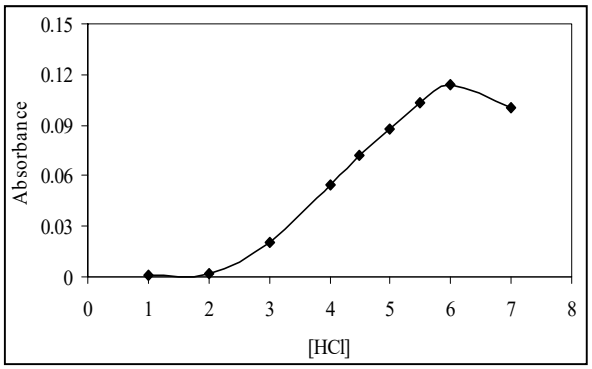


Fig. 3 Effect of HCl concentration. [Hf(IV)]: 5 µg ml^{-1}, Volume of reagent: 1 ml

C. 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 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.

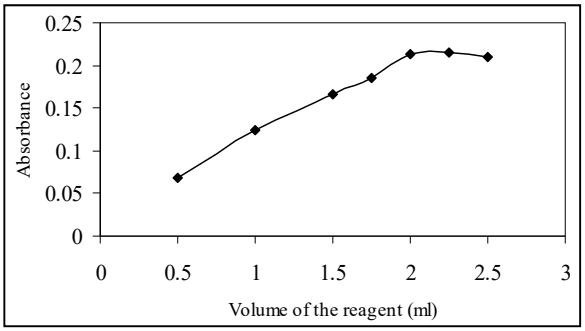


Fig. 4 Effect of reagent volume. [Hf(IV)]: 5 µg ml^{-1}, HCl concentration: 6 M

D. Rate of Reaction and Stability of the System

The reaction between Hf(IV) with reagent was completed at room temperature. Maximum and constant absorbance at 421 nm was observed within 90 min and remained constant for at least 10 h. Therefore, a standing time of 90 min was selected for the measurements.

E. Calibration Curve and Sensitivity

To determine Hf concentration, the calibration curve was plotted in optimum conditions. Within the range of 2–11 µg ml^{-1} Hf concentration, the calibration curve followed the Beer's law. The linear regression equation was: $A = 0.0719 + 0.0147C_{Hf}$ (µg ml^{-1}). The correlation coefficient was 0.998. The apparent molar absorption coefficient (ε) was 0.26×10^4 l mol^{-1} cm^{-1} calculated from the slope of calibration curve. The detection limit, lower limit of detection, or LOD (limit of detection) for Hf(IV), was estimated by $3S_b/m$ (where S_b is the standard deviation of 10 measurements of the blank solution and m is the slope of the calibration line), was measured 0.154 µg ml^{-1} for the analyte. The relative standard deviation (RSD) was used to express the precision and repeatability of an assay. For this purpose, 5 µg ml^{-1} of Hf(IV) was determined 10 times, and RSD was obtained 2.3%.

F. Interference Studies

The effect of various cations and anions on the determination of Hf(IV) was investigated (Table I). 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 II. The recoveries are close to 100% and indicate that the proposed method is helpful for the determination of Hf(IV) in the real samples.

IV. Conclusion

A new spectrophotometric method for the determination of Hf(IV) by using a new chromogenic reagent, acidic extract of *Ficus carica* tree leaves was established. This reagent showed the maximum sensitivity for Hf(IV) in 6 M hydrochloric acid. The method has the advantage of being simple, reproducible, low cost, available, selective and relatively sensitive rather than many reported methods. Finally, with the increase in environmental awareness and governmental policies, this method is a new environmentally friendly way that can be applied for the determination of trace Hf(IV) in industrial wastewater.

TABLE I
Tolerated Limit of Various Foreign Ions

Ion	*Tolerance limit (µg ml^{-1})*	*Ion*	*Tolerance limit (µg ml^{-1})*
Li^+	1500	La^{3+}	1500
Na^+	1500	Ce^{3+}	1500
K^+	1500	UO_2^{2+}	1500
Ca^{2+}	1500	Th^{4+}	1500
Mg^{2+}	1500	Ti^{4+}	1500
Ba^{2+}	1500	Fe^{3+}	2
Ni^{2+}	1500	Zr^{4+}	0.2
Co^{2+}	1500	NO_3^-	1500
Zn^{2+}	1500	I^-	1500
Cd^{2+}	1500	SCN^-	1000
Pb^{2+}	1500	CH_3COO^-	1000
Hg^{2+}	1500	SO_4^{2-}	400
Ag^+	1500	EDTA	400
Pd^{2+}	1500	$C_2O_4^{2-}$	150

TABLE II
Determination of Hf(IV) in the Water Samples by the Proposed Method

Sample	*Hf(IV) added (µg ml^{-1})*	*Hf(IV) found (µg ml^{-1})*	*Recovery (%)*
Tab water	2.00	1.96 (1.6)[a]	98
	5.00	5.05 (0.7)	101
	10.00	9.95 (1.7)	99.5
Well water	2.00	2.03 (0.9)	101.5
	5.00	4.89 (2.1)	97.8
	10.00	9.88 (1.6)	98.8
Waste water	2.00	1.92 (1.7)	96
	5.00	4.94 (1.8)	98.8
	10.00	9.83 (2.2)	98.3

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

References

[1] A. F. Holleman, E. Wiberg and N. Wiberg, Lehrbuch der Anorganischen Chemie (in German) (91–100 ed.). Walter de Gruyter. pp. 1056–1057, 1985.
[2] R. M. Wallace, R. A. Stoltz, and G. D. Wilk, Texas Instruments Inc, Zirconium and/or hafnium oxynitride gate dielectric. U.S. Patent 6,291,866, 2001.
[3] B. H. Lee, L. Kang, R. Nieh, W. J. Qi, and J. C. Lee, Thermal stability and electrical characteristics of ultrathin hafnium oxide gate dielectric reoxidized with rapid thermal annealing. Applied Physics Letters, 76(14), pp.1926-1928, 2000.
[4] E. P. Gusev, V. Narayanan, and M. M. Frank, Advanced high-κ dielectric stacks with polySi and metal gates: Recent progress and current challenges. IBM Journal of Research and Development, 50(4.5), pp.387-410, 2006.
[5] Handbook of Chemistry and Physics. 87th edition, CRC, 2006.
[6] J. D. Lee, Concise inorganic chemistry. Fifth Edition, Chapman & Hall, London, pp. 684, 1996.
[7] E. W. Spitz, J. R. Simmler, B. D. Field, K. H. Roberts, and S. M. Tuthill, Spectrographic Determination of Certain Rare Earths in Stainless Steels.

Open Science Index, Chemical and Molecular Engineering Vol:12, No:3, 2018 publications.waset.org/10008698/pdf

Analytical Chemistry, 26(2), pp.304-307, 1954.
[8] Xiwen, H., Huarui, H. and Huiming, S., 1987. Selective Spectiophotometry for Determination of Hafnium in the Precence of Zirconium by the Difference in Solution State [J]. Analytical Laboratory, 3, p.000.
[9] Clowers, C.C. and Guyon, J.C., 1969. Spectrophotometric determination of hafnium as reduced molybdosulfatohafnic acid. Analytical Chemistry, 41(8), pp.1140-1142.
[10] Clowers, C.C. and Guyon, J.C., 1969. Absorptiometric determination of hafnium with molybdophosphoric acid. Microchimica Acta, 57(5), pp.989-994.
[11] Kalyanaraman, S. and Fukasawa, T., 1983. Spectrophotometric determination of zirconium and hafnium with 4-(2-pyridylazo) resorcinol. Analytical Chemistry, 55(14), pp.2239-2241.
[12] Subrahmanyam, B. and Eshwar, M.C., 1975. Rapid extractive spectrophotometric determination of hafnium (IV) with 4-(2-pyridylazo) resorcinol. Analytical Chemistry, 47(9), pp.1692-1693.
[13] Cheng, K.L., 1959. Analytical applications of xylenol orange—III: Spectrophotometric study on the hafnium-xylenol orange complex. Talanta, 3(1), pp.81-90.
[14] Agrawal, Y.K. and Dayal, U., 1984. Spectrophotometric determination of hafnium as a mixed-ligand complex with N-p-tolyl-p-methoxybenzohydroxamic acid and xylenol orange. Analyst, 109(12), pp.1565-1567.
[15] Z. Marczenko Spectrophotometric Determination of Elements. John Wiley & Sons, New York, pp. 555, 609, 1976.
[16] S. B. Savvin, Arsenazo III. Atom Izdat, Moscow, 1966.
[17] Perkampus, UV-Vis Spectroscopy and Its Applications. Springer-Verlag, Berlin pp. 33, 1992.
[18] K. L. Cheng, Determination of zirconium and hafnium with xylenol orange and methylthymol blue. Anal. Chim. Acta, vol. 28, 41-53, 1963.
[19] B. Subrahmanyam, M. C. Eshwar, Spectrophotometric determination of hafnium(IV) with 1-(2-pyridylazo)-2-naphthol. Microchim. Acta, vol. 66, pp. 585-590, 1976.
[20] S. Kalyanaraman, and T. Fukasawa, Spectrophotometric determination of zirconium and hafnium with 4-(2-pyridylazo)resorcinol. Anal. Chem., vol. 55, pp. 2239, 1983.
[21] H. H. Perkampus, UV-VIS Spectroscopy and its Applications. Springer Science & Business Media, 2013.
[22] Stover, M. Aradhya, L. Ferguson, and C. H. Crisosto, The fig: overview of an ancient fruit. HortScience, vol. 42, pp.1083, 2007
[23] RHS A-Z encyclopedia of garden plants. United Kingdom: Dorling Kindersley. 2008. p. 1136. ISBN 1405332964.
[24] A. Eisen, The Fig: Its History, Culture, and Curing: With a Descriptive Catalogue of the Known Varieties of Figs, US Government Printing Office, (No. 9), 1901.

Open Science Index, Chemical and Molecular Engineering Vol:12, No:3, 2018 publications.waset.org/10008698/pdf