

# Spectrophotometric Determination of Zirconium and Hafnium with Uramildiacetic Acid

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**Abstract:** The reactions of Zirconium (IV) and Hafnium (IV) with uramildiacetic acid (UDA) reagent have been studied spectrophotometrically and the stoichiometries of the ternary complexes have been determined. The method has been applied for direct determination of Hf (IV) and Zr (IV) with UDA in acidic medium. The absorption has been measured between 450 - 540 nm. Beer's law is obeyed for Zr and Hf concentration of 0.1 - 5.0 µg per ml. The molar absorptivities of aqueous Zr and Hf complexes were  $1.80 \times 10^{-5}$  and  $3.1 \times 10^{-5} \text{ molL}^{-1} \text{ cm}$ . This method is simple, fairly accurate, rapid and free from interference from most common metal ions. The accuracy and precision have exhibit to be adequate for zirconmatrices.

**Keywords:** Spectrophotometer, Zirconium, Hafnium, Uramildiacetic acid, Beer's law

## 1. Introduction

Several spectrophotometric methods have been reported for the determination of metals. None of them is, however, applied to uramildiacetic acid (UDA) [1], in presence of glycine and other metal ions. The method proposed here is based on complex formation between UDA and ferric ions. Glycine also complexes with ferric ion [1, 2] but its interference can be eliminated by proper choice of pH and wavelength. Other metal ions do not interfere.

Various reagents have been proposed for the calorimetric determination of Zr (IV) and Hafnium (IV) but few reagents have been studied in details: such as arsenazo (III), chromeazchols, 6, 7, dihydroxy, 2, 4 diphenyl chromanmethyl thymol blue and xylenol orange, (1 pyridylazo) resorcinol, PAR was investigated for determination of Zr (IV) and Hf (IV). [3 - 6]. The reactions of Zr (IV) And Hf (IV) species with 4 - (2 - pyridylazo) - 2 - (PAN), arsenazo III, 4 - (2 - pyridylazo) resorcinol (PAR), 2, 4 - dihydroxy benzaldehyde isonicotinoyl hydrazone [7 and salicyl fluorine [8] were reported. The 2, 2x, 3, 4 - tetrahydroxy - 3x - sulpho - 5x - carboxazobenzene reagent and Janus green dye were also proposed. Actually, most of these methods suffer from low sensitivity and selectivity. Other reagents suggested are 5, 7 dichoro 8 hydroxy methyl quinoline, cyclopentanone 2carboxyanilide and 8 hydroxy quinoline. [9 - 10].

In this paper uramil - N, N diacetic acid (UDA: 5 amino 2, 4, 6 trioxo - 1, 3 perhydrodiazine - N, N diacetic acid) is proposed for the UV spectrophotometric determination of zirconium and Hafnium. The method developed is unusual in that, compound of the EDTA type is employed for a direct evaluation of zirconium and hafnium [11 - 13]. In acidic medium [14 - 16], the complex formed shows peak absorbance at 450 - 460nm [18]. Hafnium also forms a 1: 1 complex with UDA; in acidic medium this complex shows an absorption maximum at 520 nm. [17 - 18]

A series of synthesized reagents were tried for availability of Zr (IV) and Hf (IV) determination. This work presents a new synthesized reagent to be used for direct determination of Zr

(IV) and Hf (IV) in aqueous solution. To develop the reagent, the parameters (pH, absorption spectra, concentration of dye, etc.) that affect Zr (IV) and Hf (IV) analysis have been investigated to provide optimum conditions [19 - 20] for their determinations.

## 2. Experimental

**Apparatus:** Spectrophotometric analysis of Zr and Hf elements by Unicam UV 2100. The concentrations of other elements including (silica, total iron, etc.) were determined using the standard methods of analyses.

The zirconium standard solution was prepared by direct dissolution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (99.5%, Riedel - de Haen) in 2 mol  $\text{L}^{-1}$  HCl.

The hafnium standard solution was prepared from hafnium oxide ( $\text{HfO}_2$ , Spec pure, Johnson, Mathey). The oxide was dissolved in a  $\text{HF}-\text{H}_2\text{SO}_4$  (1: 1 v/v) mixture and completed to 100 ml with distilled water. The stock solution was diluted with water to give working solution of 40 µg/ml of Zr and 45 µg/ml of Hf.

**Uramildiacetic acid solution:** Prepare an aqueous solution by adding 0.1 M sodium hydroxide dropwise to a suspension of the pure compound in water and standardize the solution by titration with zinc (II) solution. Prepare more dilute solutions as required.

For the reagent solution (0.07 % w/v), dissolve the pure reagent in water with the aid of 0.1 M sodium hydroxide.

Buffer solutions of pH 4.0 and 4.5 were mixed to the appropriate amounts of 0.2 M sodium acetate and 0.2 M acetic acid. All other reagents were of analytical grade. Deionised distilled water was used.

**Recommended procedures:** Transfer 5.0 ml of sample solution containing sufficient Zr (IV) to give a final concentration of 0.5 - 2.2 microgram per ml to a 25 ml volumetric flask. Add 2.0 ml of 0.07 % UDA reagent and 10 ml of buffer pH 4.5 solutions. Dilute to the mark with water.

Measure the absorbance at 460 nm against a reagent blank prepared simultaneously. [21 - 23]

For the determination of Hf (IV) proceed similarly, but use sufficient sample solution to give a final concentration of 0.4 - 6.3  $\mu\text{g/ml}$ . and pH 5 buffers, and measure the absorbance at 520 nm and use the optimal concentration ranges, pH intervals and  $\lambda$  max mentioned below.

### 3. Results and Discussion

#### Absorption spectra

The absorption spectra of (Zr (IV) and Hf (IV)) complexes of UDA in U. V. range at different pH values is shown in

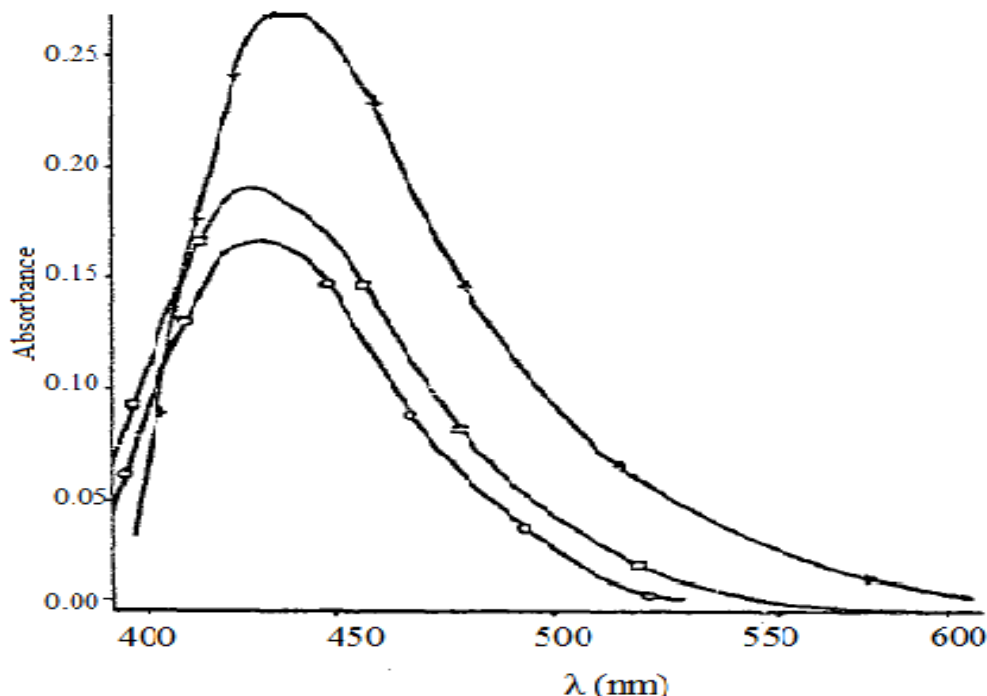
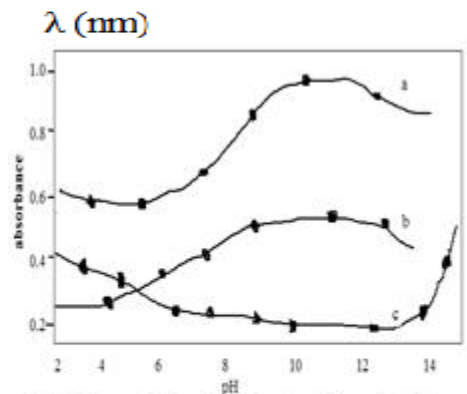


fig.1. For the zirconium (IV) complex, the absorption maximum is at 460 - 465 nm in the pH range 3.2 - 5.2 absorbances become negligible at high pH values. For the Hafnium (IV) complex, the absorption maximum is at 520 nm in the pH range 4.5 - 6.4; again the complex decomposes at high pH. The behaviour of some other metal—UDA chelates is similar in the U. V. range. Fig.1. Absorption spectra for the Zirconium (IV) —UDA system. 0.51  $\mu\text{g Zr mL}^{-1}$ , pH 3.2; 0, pH 4.2; 0, pH 5.2.

**Effect of experimental variables** Tests were made with solutions containing 0.50  $\mu\text{g mL}^{-1}$  Zr or 4.0  $\mu\text{g mL}^{-1}$  Hf. When the pH of the mixtures was adjusted with hydrochloric acid or sodium hydroxide, constant absorbance was found over the pH ranges 3.5 - 4.5 (Zr) and 4 - 6 (Hf); the absorbance decreased rapidly outside these ranges.

The volumes of 0.05 % UDA solution required to react with the above concentrations of metal ion were 0.5 and 1.0 ml, respectively. To ensure complete formation of the chelates over the specified ranges, 2.0 ml of UDA solution is recommended. The reactions are immediate, and the order of addition of the reagents is not critical.



Effect of pH on complex formation: (a) Zirconium-UDA complex at 540 nm vs reagent blank,  $[\text{Zr(IV)}] = 1.5 \times 10^{-5} \text{ M}$ ;

(b) Hafnium(IV)-UDA complex at 530 nm vs reagent blank,  $[\text{Hf(IV)}] = 4.5 \times 10^{-5} \text{ M}$ ; (c) UDA at 535 nm vs water,  $[\text{UDA}] = 4.5 \times 10^{-3} \text{ M}$

The Zirconium (IV) and the Hafnium (IV) complex could be heated at high temperature without the absorbance being affected, and the Hafnium (IV) complex to 100 °C. The stability of the complexes was excellent, the absorbance being unaffected by standing for up to 3 d and 2 d, respectively.

#### Beer's law, molar absorptivity and sensitivity:

Beer's law is obeyed over the ranges 0.1 - 5.0  $\mu\text{g mL}^{-1}$  of Zr and 0.2 - 10.0  $\mu\text{g mL}^{-1}$  Hf  $\mu\text{g mL}^{-1}$ . For 10 - mm optical

cells, the optimal concentration ranges are 0.5 - 2.0  $\mu\text{g mL}^{-1}$  Zr and 0.5 - 6.5  $\mu\text{g mL}^{-1}$  Hf. Under the recommended conditions, the molar absorptivities and Sandell sensitivities are  $1.80 \times 10^{-5} \text{L mol}^{-1} \text{cm}^{-1}$  and  $0.005 \text{L mol}^{-1} \text{cm}^{-1}$  for the Zirconium (IV) complex, and  $3.0 \times 10^{-5} \text{L mol}^{-1} \text{cm}^{-1}$  and  $0.010 \mu\text{g cm}^{-2}$  for the Hafnium (IV) complex. The reproducibility is good; the standard deviation is about 1 % for the range 0.150 - 0.500 absorbance unit (10 determinations each of four metal ion concentrations over the range).

**Effect of foreign ions.** Various amounts of foreign ions were added to solutions containing 0.5  $\mu\text{g Zr mL}^{-1}$  or 5.0  $\mu\text{g Hf mL}^{-1}$ , and the recommended procedures were followed. Chloride, bromide, iodide, acetate, citrate, phosphate, perchlorate, arsenate and oxalate in 100 - fold amounts, and nitrate, nitrite, thallium (I) and chromium (III) in 10 - fold amounts do not interfere in the Zirconium determination. The tolerances are the same in the Hafnium determination, except that oxalate interferes at 10 - fold concentrations, and thallium (I) and chromium (III) interfere at concentrations greater than 10 % that of cobalt. Tungstate, dichromate, zinc, cadmium, nickel, manganese (II), iron (III), cerium (IV), vanadium (V), lead (II), palladium (II) [24 - 25] and uranyl ions interfere with the Zirconium determination if present in concentrations greater than 20 % that of Zirconium and interfere with the Hafnium determination if present in concentrations exceeding 10 % that of cobalt. Because the tolerances for these metal ions are so small, prior separations are essential.

The isolation of the metals before their determination can be achieved by ion exchange or by solvent extraction; the former is probably more appropriate, particularly if chelating resins of the iminodiacetic acid type are used, because high concentration factors can be achieved, and there is less possibility of contamination from reagents.

#### Determination of other metals

Some other metals can also be determined in acidic solutions with UDA as reagent. Thus titanium (IV) reacts with UDA at about pH 2 to give a chelate with  $\lambda_{\text{max}}$  458 nm and a molar absorptivity of  $8.3 \times 10^3 \text{L mol}^{-1} \text{cm}^{-1}$  (optimal range 1.35 - 7.20  $\mu\text{g Ti mol}^{-1} \text{cm}^{-1}$ ).

#### Stoichiometry of the reactions

The molar ratio and continuous variations methods showed that 1: 1 complexes were formed between UDA and the metal ion. In the molar ratio method, a fixed concentration of  $2.50 \times 10^{-3} \text{M}$  Zirconium (IV) or  $1.05 \times 10^{-3} \text{M}$  Hafnium (IV) was used. For Job's method, total concentrations of  $10.7 \times 10^{-4} \text{M}$  and  $5.0 \times 10^{-4} \text{M}$  were used for Zirconium study and  $10.5 \times 10^{-4} \text{M}$  and  $2.0 \times 10^{-4} \text{M}$  for the Hafnium work. The other metal ions mentioned above also form 1: 1 complexes.

## 4. Conclusion

The spectrophotometric procedure described permits the direct determination of zirconium or hafnium content. A simple analytical procedure, using the reagent UDA, was established for determining the zirconium or hafnium complex ion alloys. Neither molybdenum, nor titanium

interfered with the colour complex. Repetitive analyses showed good agreement. This indicates that the outlined analytical procedure is capable of yielding reproducible analytical values.

## References

- [1] U. D. Uysal, A. A. Huseyinli, T. Guray; *Journal of Scientific & Industrial Research*, **70**, 45 (2011). Rapid direct spectrophotometric determination of zirconium (IV) in alloys with 2, 2., 3, 4 - tetrahydroxy - 3 - sulpho - 5 - chloroazobenzene.
- [2] Rajendra Prasad & Surendra Prasad; *J. of Chemical Education*, **86** (4), 494 - 497, 2009. Spectrophotometric determination of Iron (III) glycine formation constant in aqueous medium using competitive ligand binding.
- [3] A. Tupys, O. Tymoshuk, and P. Rydchuk; *Chemistry and Chemical Technology*, vol.10, (1) 19-25, 2016. Spectrophotometric investigation of Cu (II) ions interaction with 1 - (5 - benzylthiazol - 2 - yl) azonaphthalen - 2 - ol.
- [4] A. Ashton, A. G. Frogg, D. T. Burns; A highly selective direct colorimetric procedure for the determination of zirconium in steel with arsenazo III using a pressure digestion technique for dissolution, *Analyst*, **99**, 108 (1974).
- [5] B. Subrahmanyam, M. C. Eshwar; *Mikrochimica Acta*, **66**, 585, (1976). Spectrophotometric determination of Hafnium (IV) with 1 - (pyridylazo) - 2 - naphthol.
- [6] O. Takashi; *Geostand. News*, **21** (1), 97 (1997). Determination of zirconium in carbonate rock reference materials with xylenol orange spectrophotometric method. S. Kalyanaraman, T. Fukasawa; Spectrophotometric determination of zirconium and hafnium with 4 - (2 - pyridylazo) resorcinol, *Anal. Chem.*, **55**, 2239, (1983).
- [7] S. Sivaramaiah, P. R. Reddy, V. K. Rey, T. S. Reddy; *Indian J. chem. Inorg. Phys. Theor. Anal. Chem*; **42**, 109 (2003). Direct & derivative spectrophotometric determination of Zirconium (IV) with 2, 4 dihydroxy benzaldehyde isonicotinoyl hydrazone.
- [8] S. Kumiyo, M. Yoshimi, T. Kumiko, K. Shinichiro, F. Tsuyoshi, Y. Takako, F. Yoshikazu; **56**, 773 - 779 (2007). Spectrophotometric determination of zirconium (IV) and fluoride ion using color reaction among salicyl fluorone, zirconium (IV) and fluoride ion, *Bunseki Kagaku*,
- [9] T. A. Lasheen, G. M. Hussein, Y. M. Khawassek, M. F. Cheira; *ACAIJ*, **12** (10), 368 - 376 2013. Spectrophotometric determination of zirconium (IV) and hafnium (IV) with pyrazolo (1, 5 - a) quinazolin - 6 - one derivative reagent
- [10] O. Tymoshuk, L. Oleksiv, L. Khvalbota, T. Chaban, and I. Patsay, "Spectrophotometric determination of Ru (IV) using 5 - hydroxyimino - 4 - imino - 1, 3 - thiazolidin - 2 - one as a novel analytical reagent," *Acta Chimica Slovenica*, vol.66, no.1, pp.62-69, 2019.
- [11] P. P. Zamora, J. W. Martins; *Talanta*, **49**, 937 - 941 (1999). Anomalies in the spectrophotometric and extractive behaviour of zirconium and hafnium - Evidence of a synergistic effect.
- [12] N. A. Mohammed, A. M. Daher; *Hydrometallurgy*, **65**,

- 103 - 107 (2002). Preparation of high purity zirconia from Egyptian zircon: anion - exchange purification process.
- [13] S. L. Narayana, K. J. Reddy, S. A. N. Reddy, J. R. Kumar, and A. V. Reddy, *Journal of the Chinese Chemical Society*, vol.54, no.5, pp.1233–1241, 2007. Synthesis of new reagent benzyloxy benzaldehyde thiosemicarbazone (BBTSC): selective, sensitive and extractive spectrophotometric determination of Pd (II) in water samples and synthetic mixtures. .
- [14] O. Tymoshuk, O. Fedyshyn, L. Oleksiv, A. Oliinyk, and V. Matychuk, *Visnyk of the Lviv University. Series Chemistry*, vol.60, no.1, pp.210–217, 2019. Spectrophotometry of 4 - (4 - imino - 2 - oxo - thiazolidine - 5 - ilazo) - benzoic acid.
- [15] L. Lozynska, O. Tymoshuk, and T. Chaban, *Acta Chimica Slovenica*, vol.62, no.1, pp.159–167, 2015. Spectrophotometric studies of 4 - [N' - (4 - imino - 2 - oxo - thiazolidin - 5 - ylidene) - hydrazino] - benzenesulfonic acid as a reagent for the determination of palladium.
- [16] Y. K. Agrawal, M. Sanyal, P. Shrivastav, S. K. Menon; *Talanta*, 46, 1041 (1998). Sequential liquid - liquid extraction graphite furnace atomic absorption spectrometric (GFAAS) and spectrophotometric determination of zirconium (IV) with calixarene hydroxamic acid.
- [17] H. Z. Li, C. X. Yang and D. T. Zhai, *Spectrosc. Spectr. Anal.*, 25, 283, 2005.
- [18] N. Hassan and A. S. Amin, *Analytical Chemistry Letters*, vol.7 (5), 724–736, 2017.
- [19] H. Bagheri, M. S. Tehrani, M. R. Shishehbore, M. Shahvazian; *Prog. Color Colorants Coat*, 3, 58.2010. Janus green dye as a new reagent for catalytic kinetic determination of zirconium in ceramic materials.
- [20] R. F. Gur'eva and S. B. Savvin, vol.57, no.11, pp.980–996, 2002. "Spectrophotometric methods for determining noble metals, " *Journal of Analytical Chemistry*.
- [21] Christian G. D., *Analytical Chemistry*, New York: John Wiley & Sons, Inc. (1994).
- [22] Dean J. A., *Analytical Chemistry Handbook*, New York: McGraw - Hill, Inc. (1995).
- [23] Q. H. Huang and H. Y. Yang, *Metal. Anal.*, 28, 55 (2008).
- [24] S. H. Gaikwad, T. N. Lokhande, and M. A. Anuse, *Indian Journal of Chemistry*, vol.44A, 1625–1630, 2005. Extraction spectrophotometric determination of micro amounts of palladium (II) in catalysts.
- [25] Y. Q. Wu and H. Xu, *Phys. Test. Chem. Anal., Part B: Chem. Anal.*, 41, 28, (2005)