



Development of an Extractive Spectrophotometric Method for Determination of Zr(IV) Using 2, 4-Dimethyl -3H- 1, 5 Benzodiazepine

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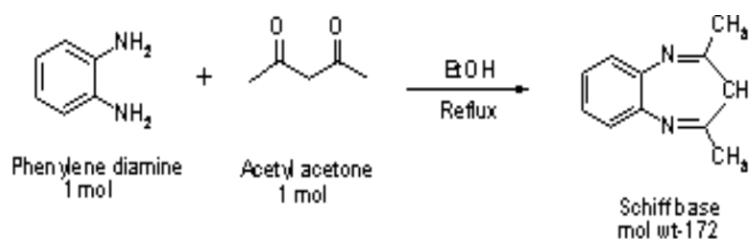
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ABSTRACT

A new analytical reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) is proposed for the extraction and spectrophotometric determination of Zr (IV). The Reagent was synthesized and characterized by IR, NMR, elemental analysis as well as Mass spectrometry. DBA reacts with Chromium to give red colored complex which can be quantitatively extracted into n-butanol at pH 8.8. The organic extract shows maximum absorption at 500nm where absorption due to similarly prepared reagent blank is negligible. The beer's law is followed in the concentration range 1-10 $\mu\text{g mL}^{-1}$ of Zr (IV). The molar absorptivity and Sandell's sensitivity of Zr (IV)-DBA complex is 7460 $\text{Lit mol}^{-1}\text{cm}^{-2}$ and 0.02427 $\text{mg cm}^{-2}\text{L}^{-1}$ respectively. The proposed method is rapid, sensitive, reproducible, and accurate and has been satisfactory applied for determination and separation of Zirconium (IV) in commercial mixtures, pharmaceutical samples and alloys.

Graphical Abstract:



Synthesis of Reagent 2, 4-DIMETHYL -3H- 1,5 BENZODIAZEPINE (DBA)

Keywords: Zirconium (IV), Spectrophotometric determination, DBA reagent.

INTRODUCTION

The symbol of Zirconium is Zr and atomic number 40, is lustrous grey-white, strong transition metal that resembles Titanium. Zirconium is mainly used as a refractory and opacifier, although it is used in small amounts as an alloying agent for its strong resistance to corrosion. Zirconium forms a variety of Inorganic and organometallic compounds such as zirconium dioxide and zirconocene dichloride respectively. Five isotopes occur naturally, three of which are more stable. Zirconium compounds have no known biological

role; zirconium is a lustrous, grayish white, soft ductile and malleable metal which is solid at room temperature, though it becomes hard and brittle at lower purities. In powder form, zirconium is highly flammable, but the solid form is far less prone to ignition. Zirconium is highly resistant to corrosion by alkalis, acids, salt water and other agents. However, it will dissolve in hydrochloric and sulphuric acid, especially when fluorine is present. Alloys with zinc become magnetic below 35K.

Melting point of zirconium is 1855⁰C (3371⁰F), and its boiling point is 4371⁰C (7900⁰F). Zirconium has electronegativity of 1.33 on Pauling scale of the elements within d-block, zirconium has the fourth lowest electronegativity after yttrium, lutetium and hafnium. At room temperature zirconium exhibits a hexagonally close packed crystal structure, α -zirconium, which changes to β -zirconium a body centered cubic crystal structure at 863⁰C. Zirconium exists in the beta phase until the melting point $ZrZn_2$ is one of only two substances to exhibit superconductivity and ferromagnetism simultaneously with the other being UGe_2 . Zirconium occurs in nature as the mineral zircon ($ZrSiO_4$). Its hardness and useful properties, such as the ability to increase corrosion resistance and mechanical strength of alloys at low and elevated temperature, have made its determination important in special steels and alloys.

Also, its transparency to thermal neutrons has made zirconium a good construction material in nuclear reactors [1, 2]. The direct determination of Zr (IV) in alloy and other samples is of great importance in analytical point of view. There are numerous methods outlined for determination of Zr(IV) in literature [3-9]. Trace amounts of zirconium have been determined by X-ray fluorescence, neutron activation, atomic emission and spectrophotometry [10-14].

Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity. Many methods of zirconium determination have been published [1, 3-6]. However, some of these methods have both low sensitivity and low selectivity while others have high sensitivity but low selectivity in presence of some ions or molecules. [2,18,19]. Arsenazo-III, Alizarin S, pyrocatechol violet and xylenol orange, PAR, Picramine P, Br-PADAP, 5,7-dibromo-8-hydroxyl quinoline, 2,2',3,4'- tetrahydroxy-3'-sulpho-5'-carboxyazobenzene, 4,5-dihydroxybenze-1,3-disulfonic acid disodium salt and chrome azurol-S have all been proposed to be good ligands for determination of zirconium [17- 18]. Determination of zirconium with alizarin S, pyrocatechol violet, and xylenol orange is carried out after separating interfering species. So, these methods have low sensitivity and low selectivity [15, 20] Solid-phase spectrophotometry was used to determine trace amounts of Zr(IV) in water, soil, plant materials and ore samples. Zr(IV) was sorbed in a dextran-type lipophilic gel as a complex with 2-(2-benzothiazolylazo)- 3-hydroxyphenol [21-26].

MATERIALS AND METHODS

Instruments: A Shimadzu 2450 UV-Visible spectrophotometer with 1.0 cm quartz cell was used for absorbance studies. An Elico LI-120 digital pH-meter was used for pH adjustments. The experimental conditions are maintained as presented in Table 1.

Table 1. Experimental conditions

Condition	Results
Absorption Maxima	500nm
Solvent	n- butanol
pH range	8.8
Equilibration time	10 seconds
Stability of Chromium- reagent	36 hours
Beer's range	1 to 10 mg/cm ³
Molar absorptivity	7460 Lit mol ⁻¹ cm ⁻²
Sandell's sensitivity	0.02427 mg/ cm ²
Mole ratio of Cr: reagent	1:1

Synthesis of Reagent: The reagent was synthesized by mixing 1 mole of O phenylenediamine and 2 moles of Acetyl acetone in Ethanol. The above mixture is refluxed for 2h in round bottom flask. The solution thus obtained is poured in ice. Solid is formed, which is purified with ethanol. It is then characterized and used for extractive spectrophotometric determination of Zr (IV). A stock solution of reagent with concentration 0.05% was prepared in methanol. The scheme of reaction is as shown in figure1.

Reaction

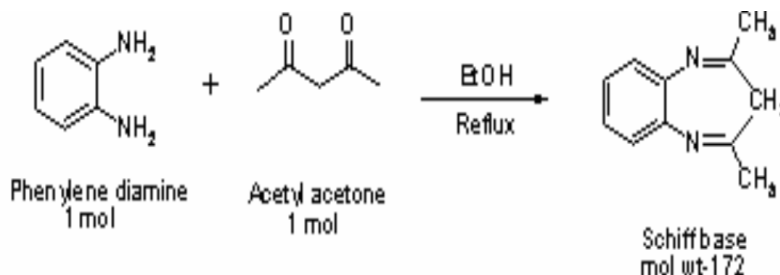


Fig.1 Synthesis of Reagent 2, 4-DIMETHYL -3H- 1,5 BENZODIAZEPINE (DBA)

Preparation of stock solution: A weighed quantity of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in double distilled water then diluted to desired volume by double distilled water.

Extraction as a function of pH: The extraction of Zirconium was carried out at various pH conditions ranging from the pH 1 to pH 11 using various buffer solutions. The ratio of organic phase to aqueous phase was kept 1:1. The present extraction was observed to be quantitative at pH 8.8. Therefore pH 8.8 was selected for further studies and presented in figure 2.

Effect of solvent: The suitability of extraction was studied using various organic solvents such as n-butanol, toluene, cyclohexanone, cyclohexanol, chloroform, ethyl acetate, carbon tetrachloride, xylene, diethyl ether and hexane. The extraction of chromium was observed to be quantitative in the organic solvent n-butanol. Therefore n-butanol is used for extraction of Zirconium. Figure 3 indicate that n-butanol is observed to be an appropriate solvent.

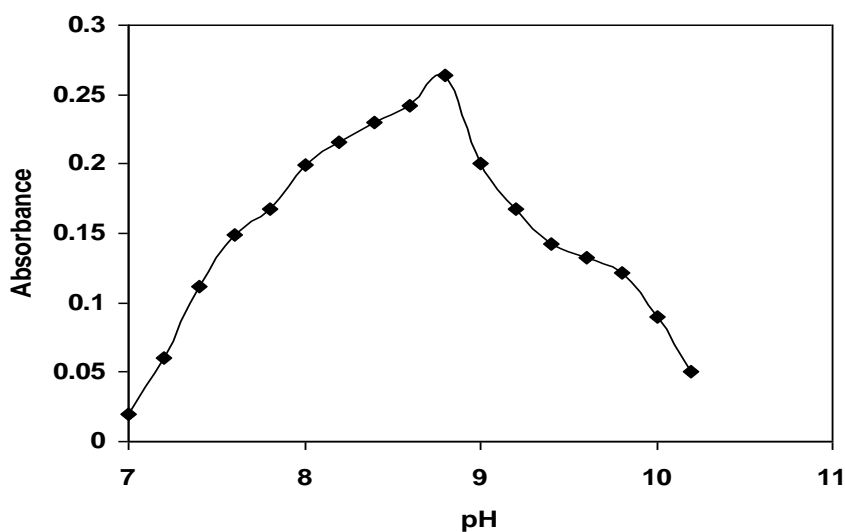


Fig 2. Extraction as a function of pH

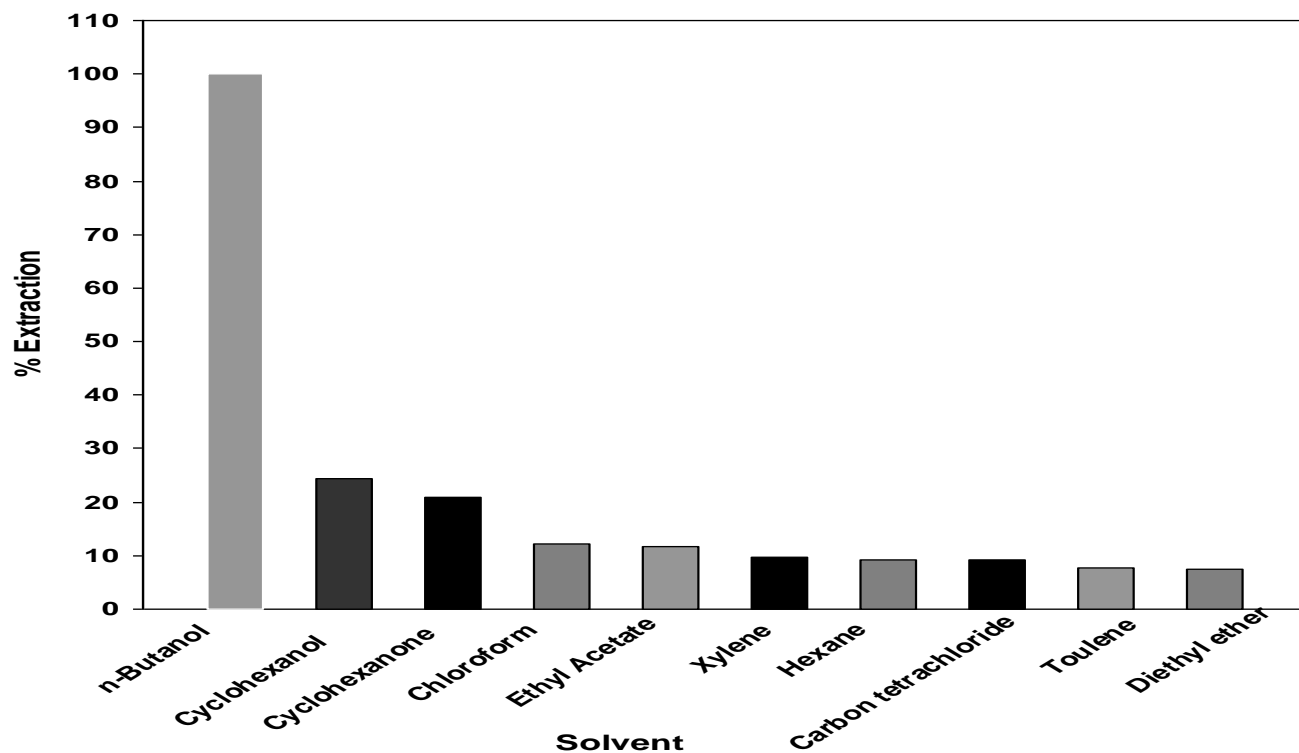


Fig 3. Effect of solvent

Absorption spectrum: Fig.4 depicted that the absorption spectrum in n-butanol observed to be maximum absorption at 500 nm and the absorption due to reagent was found to be negligible at this wavelength. Hence 500 nm was selected as wavelength for the absorbance measure in the spectrophotometric determination of zirconium against reagent blank.

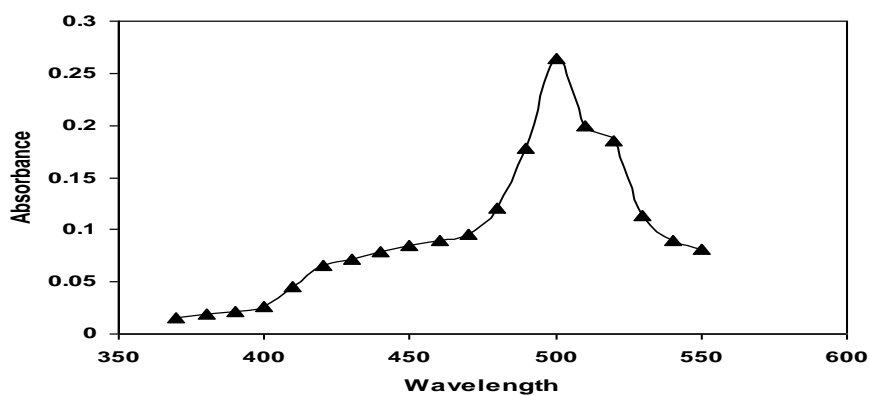


Fig 4. Wavelength of absorption

Recommended procedure: Mix 1 cm³ aqueous solution containing 1-100mg of Zirconium and 1cm³ of 0.05% methanolic solution of reagent in 25 cm³ beaker. Adjust the pH of the solution to required value with buffer solution Make the final volume 10 cm³. Transfer the solution into 125 cm³ separating funnel and equilibrate for 1min with 10 cm³ n- butanol. Allow the two phases to separate and measure the absorbance of organic phase containing the complex at 500 nm against reagent blank.

RESULTS AND DISCUSSION

Preparation of calibration plot: The calibration curve was prepared by taking known amount of zirconium which was treated as described in the procedure. A graph of absorbance against concentration was prepared (Fig.2). The concentration of the unknown zirconium solutions is determined from the calibration plot as presented in Fig.5.

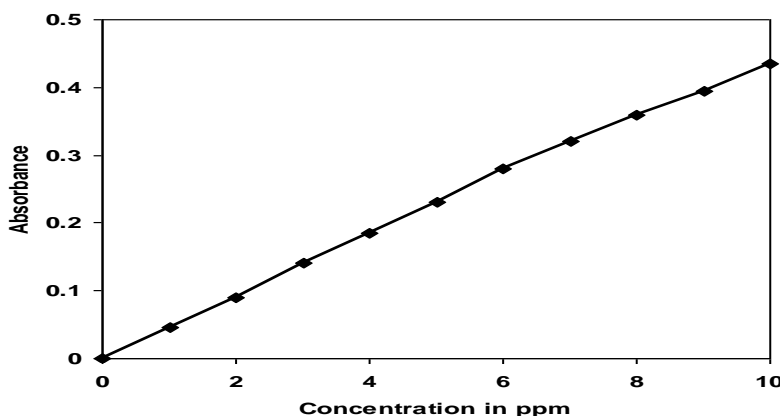


Fig 5. Calibration Plot of Zr (IV) in mg mL^{-1} against Absorbance

Composition of the extracted species: The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Zr (IV): DBA reagent is 1: 1 and above results are confirmed from Fig.6.

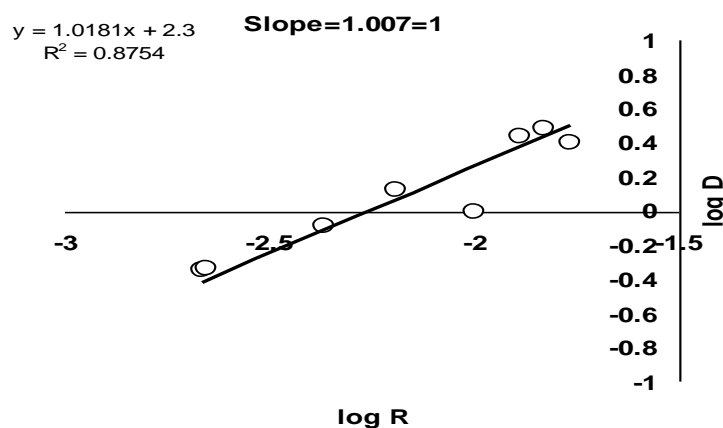


Fig 6. Slope Ratio method

Effect of foreign ions: The effect of diverse ions on the Zirconium (IV) determination was studied, in presence of a definite amount of a foreign ion. Various cations and anions were investigated in order to find the tolerance limit of these foreign ions in the extraction of Zirconium (IV) as presented in Table 2. The tolerance limit of the foreign ion was taken as the amount required causing an error of not more than 2% in recovery of Zirconium (IV). The ions which interfere in the spectrophotometric determination of Zirconium were masked by using appropriate masking agents as presented in Table 3.

Table 2. Effect of foreign ions

S. No.	Interfering ions	Tolerance limit
1	Acetate, Oxlate, CN ⁻ , I ⁻ , Br ⁻ , NO ₃ ⁻ , Cl ⁻ , BrO ₃ ⁻ , ClO ₃ ⁻ , IO ₃ ⁻ , NO ₂ ⁻ , SO ₄ ⁻ , SO ₃ ⁻	22
2	Tartarate	16
3	phosphate	14
4	Mg(II), Zn(II), Mo(VI), Ce(IV), Bi(III), Ca(II), As(III), Pb(II), Al(III),	18
5	V(V), Cd(II)	10
6	Na ⁺ , Ag ⁺	18
7	Fe(II), Ni(II), Mn(II), Cr(II), Co(II), Fe(II), Cu(II), EDTA	Interfere strongly

Table 3. Masking agents

Interfering Ion	Masking agent added	Interfering Ion	Masking agent added
Cd (II)	Potassium Iodide	EDTA	Boiled with concentrated HNO ₃
Fe (III)	Thiourea	CN ⁻	Boiled with concentrated HNO ₃
Ce (IV)	Sodium flouride	Ni (II)	Thiourea
Cr (VI)	Ammonium acetate	Cr (IV)	Sodium flouride
Mn (II)	Sodium flouride	Tartate	Sodium molybdate
Ag +	Potassium Iodide	V (V)	Thiourea

Comparison between reagents: Various reagents were investigated by the earlier researchers for removal of Zirconium (IV). The proposed reagent 2, 4-dimethyl -3H- 1, 5 benzodiazepine (DBA) is found more superior as that of reported reagents and are presented in Table 4.

Table 4. Comparison between reagents

Name of the Reagent	Limitations
5,7-dibromo-8-hydroxyquinoline	Large number of ions interfere
Polyethylene glycol- arsenazo III	1:2 complex is formed
5-chloro-8-hydroxy-7-iodoquinoline	Chloroform is used as solvent
4,5-dibromophenylfluorone	The colour development is completed at 65 ^o C
Alizarin red	Sulphate and fluoride interfere strongly

APPLICATIONS

The present method was applied for determination of amount of zirconium (IV) in various samples of alloys; commercial mixtures etc. are in well agreement with standard methods as shown in Table 5. Every result is average of independent determinations.

Table 5. Applications

S. No.	Sample	Amount of Zr(IV) in standard method	Amount of Zr(IV) in present method
1	Zirconium Silicate	85.87%	86.90%
2	Zirconium Oxide	40.08 %	40 %
3	Zr(IV)(5) + Al(III)(5)	4.90 ppm	4.97 ppm
4	Zr(IV)(5) + W(VI)(5)	5.00 ppm	4.98 ppm
5	Zr(IV)(5) + Cu(II)	4.99 ppm	5.01 ppm

CONCLUSIONS

The results obtained show that the newly developed method in which the reagent 2,4-DIMETHYL -3H-1,5 BENZODIAZEPINE (DBA) was synthesized, can be used for quantitative estimation of Zr(IV). The proposed novel reagent is found to be more effective over reported reagent from earlier investigators. The proposed method is simple, rapid and requires less volume of organic solvent. The method is also precise, less time consuming and easily employed anywhere as does not require sophisticated instruments.

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REFERENCES

- [1] H. Loh, S. Ng, M. Ahmad, M. Taib, Accurate Zirconium Detection at Visible Wavelength Using Artificial Neural Network, *Anal. Letter*, **2005**, 38, 1305-1311.
- [2] S. Oszwaldowski, J. Jakubowska, Simultaneous determination of zirconium and hafnium as ternary complexes with 5-Br-PADAP and fluoride using solid-phase extraction and reversed-phase liquid chromatography, *Talanta*, **2003**, 60, 643- 652.
- [3] A. Abbaspour, L. Baramakeh, Simultaneous determination of zirconium and molybdenum by first-derivative spectrophotometry, *Anal. Sci.*, **2002**, 18, 1127-1130.
- [4] A. Abbaspour, L. Baramakeh, Dual-wavelength beta-correction spectrophotometry for selective determination of Zr, *Talanta*, **2002**, 57, 807 -812.
- [5] A. Hüseyinli, F. Köseoğlu, U. Ülkü Dilek, Rapid Spectrophotometric Determination of Zirconium(IV) with 2,2,3,4-tetrahydroxy-3/-sulpho-5/- chloroazobenzene in Alloys., *Anal. Sci.*, **2001**, 17, 1793-1796.
- [6] H. Ronghuan, W. Jianhua, A Novel Catalytic Procedure for the Determination of Ultratrace Zirconium, *Acta*, **2001**, 137: 7-11.
- [7] K. Norisuye, H. Hasegawa, S. Mito, Y. Sohrin, M. Matsui, A method for preconcentrating Zr from large volumes of seawater using MnO₂-impregnated fibers, *Talanta*, **2002**, 53, 639-644.
- [8] S. Oszwadowski, R. Lipka, M. Jarosz, Simultaneous determination of zirconium and hafnium as ternary complexes with 2-(5-bromo--pyridylazo)-5-diethylaminophenol and fluoride by reversed-phase liquid chromatography, *Anal. Chim. Acta*, **1998**, 361, 177-187.
- [9] Z. Klima, A chemical concentration method for the determination of niobium, zirconium and tantalum in carbon steel by X-ray fluorescence spectrometry, *Analyst*, **1973**, 98, 351- 357.
- [10] G. Kirkbright, R. D. Snook, R. D. Volatilization of refractory compound forming elements from a graphite electrothermal atomization device for sample introduction into an inductively coupled argon plasma, *Anal. Chem.*, **1979**, 51, 1938-1941.
- [11] H. Uchida, T. Uchida, C. Iida, Determination of minor and trace elements in silicate rocks by inductively coupled plasma emission spectrometry, *Anal. Chim. Acta*, **1980**, 116, 433-436
- [12] H. Uchida, K. Iwasaki, K. Tanaka, Determination of traces of zirconium in silicate rocks by inductively-coupled plasma emission spectrometry, *Anal. Chim. Acta*, **1982**, 134, 375-378.
- [13] K. Grudpan, M. Utamong, C.G. Taylor, Determination of zirconium with Xylenol Orange by flow injection spectrophotometry: Application to eluates from technetium-99m generators, *Anal. Comm.*, **1998**, 35, 107-108.
- [14] A.A. El-Sayed, M.M. Hamed, S.A. El-Reefy, Determination of Micro-Amounts of Zirconium in Mixed Aqueous Organic Medium by Normal and First-Derivative Spectrophotometry, *J. Ana. Chem.*, **2010**, 65, 1113-1117.

- [15] E. Bagda, M. Tuzen, Determination of zirconium in water, dental materials and artificial saliva after surfactant assisted dispersive ionic liquid based microextraction, *RSC Adv.*, **2015**, 5, 107872-107879.
- [16] U.D. Uysal, A.A. Huseyinli, T. Güray, Rapid direct spectrophotometric determination of zirconium(IV) in alloys with 2,2,3,4-tetrahydroxy-3-sulpho-5-carboxyazobenzene reagent, *J. Sci. Ind. Res.*, **2011**, 70, 45-50.
- [17] A.A. El-Sayed, M.M.Hamed, Developed Method for Low Concentration Determination of Uranium, *Eurasian J. Anal. Chem.*, **2009**, 4, 36-45.
- [18] A.A. El-Sayed, M.M.Hamed, S.A. El-Reefy, Off-line preconcentration for determination trace amounts of niobium (V) using benzoquinone derivative as a new reagent, *Anal. Chem. Indian J.*, **2016**, 15, 93-99.
- [19] R.L. Bertolacine, J.E. Barney, Ultraviolet Spectrophotometric Determination of Sulfate, Chloride, and Fluoride with Chloranilic Acid, *Anal. Chem.*, **1958**, 30, 202-205.
- [20] P.J. Lucchesi, S.Z. Lewin, J.E. Vance, Colorimetric Determination of Strontium with Chloranilic Acid, *Anal. Chem.*, **1954**, 26, 521-523.
- [21] J. Ramkumar, Synthesis and characterization of lanthanum chloranilate complex: Application to spectrophotometric determination of anions, *Talanta*, **2006**, 68, 902-907.
- [22] S. Sander, W. Wagner, G. Henze, Direct determination of uranium traces by adsorptive stripping voltammetry, *Anal. Chim. Acta*, **1995**, 305, 154-158.
- [23] N.B.Patel, Synthesis of an Analytical Reagent, its Spectroscopic Characterization and Studies of its Complexation Behavior with Copper Metal Ion, its Application, *J Applicable Chem.*, **2017**, 6(1), 19-25.
- [24] V.J.Ghodvinde, S.M.Pitale, S.P.Janwadkar, P.P.Lohani, P.K.Rana, D.K.Yadav, New analytical technique for determination of trace amount of Fe(III) by using UV-Visible spectrometric method with photometric reagent, *J Applicable Chem*, **2017**, 6(1), 107-114.
- [25] S.R.K.Reddy, M.Rameshwara Rao, N Divanna, K.B.Chandrasekhar, Determination of Palladium (II) using cinnamaldehyde Isonicotinoyl Hydrazone by Derivative Spectrophotometric Technique, *J Applicable Chem.*, **2016**, 5(2), 375-383.
- [26] P.J.Shah, N.B.Patil, 2-4 Dihydroxy-5-Bromo Hexaphenone Oxime (DHBHPO) as a Gravimetric and Spectrophotometric Reagent: Studies on MO(VI) Complex, *J Applicable Chem.*, **2017**, 6(4), 620-627.

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