RSC Advances

RSC Advances

ARTICLE

Determination of zirconium in water, dental materials and artificial saliva after surfactant assisted dispersive ionic liquid based microextraction

Esra Bağda[a†], Mustafa Tuzen[b]

In this study, an extractive spectrophotometric method is proposed for the determination of trace amount of zirconium. The method is based on the complex formation between zirconium and 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol. Then, the formed complex is concentrated in ionic liquid (1-Hexyl-3-methylimidazolium hexafluorophosphate) phase. The parameters were optimized and analytical figures of merit were obtained. The tolerance limit for diverse ions were calculated. Enhancement factor (EF) and limit of detection (LOD) were found 156 and 0.012 µg L^{-1}, respectively. The relative standard deviation (RSD) was found lower than 6 %. The proposed method has been successfully applied to water and environmental materials.

Introduction

Zirconium is an important element. It increases corrosion resistance and mechanical strength of alloys [1]. Besides, it is used in nuclear industry, in pigment industry and as catalyst in organic reactions [2], in vacuum tubes, surgical appliances, photoflash bulbs, explosive primers, rayon spinnerets, lamp filaments [3]. In recent years the usage of zirconium oxide in dental materials became widespread due to its bio-inert non-resorbable, biocompatible characteristics [4]. According to Sollaza et al. [4], ZO dental implants show excellent corrosion resistance and a high wear resistance. An esthetically important point of the material is that zirconium oxide based dental materials have similar color to the color of natural tooth, makes it useful in esthetically important areas of the oral cavity [4]. The widespread usage of zirconium in industry and in medicinal area made scientist to develop new simple, sensitive and accurate method.

There are still existing methods and instruments for determination of zirconium, some of them are: Atomic absorption spectrometry (AAS) [5], inductively coupled plasma mass spectrometry (ICP MS) [6-8], X ray spectrophotometry [9], potentiometry [10], spectrophotometry [11, 3]. The main drawback of the instruments stated above is requirements of high operation cost and professional specialists. Among the methods, UV visible spectrophotometry is the simplest choice, and with adequate chromogenic reagents, highly sensitive and accurate results can be obtained. There are some organic

a. Faculty of Pharmacy, Cumhuriyet University, 58140 Sivas, Turkey
b. Faculty of Science and Arts, Chemistry Department, Gaziosmanpasa University, 60250 Tokat, Turkey
† Corresponding author, E-mail: esraer@cumhuriyet.edu.tr (E. Bagda)

reagents for UV vis spectrophotometric determination of zirconium: xipamide [3], 5,7-dibromo-8-hydroxyquinolinein [12], eriochrome cyanine R [13], 2-(5-Bromo-2-pyridylazo)-5-(diethylamino) phenol [14], neothoron [15], 2-(1-hydroxy-4,6-dinitro-2-phenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate (picramine ca) [16], xynelol orange [17, 18], 8-hydroxyquinoline [19], 2, 2 ' , 3, 4-tetrahydroxy-3 ' -sulpho-5 ' -carboxyazobenzene (tetrahydroxyazon SC) [20], 4-(2-pyridylazo)-resorcinol [21], Chrome Azurol S (CAS) [22]. Spectrophotometric determinations are a good preference due to their simplicity, easy operation and low operation cost. However, most analytes found in only micro or nanograms per liter or lower, than some sample preparation techniques are generally unavoidable. Solid phase extraction is one of " old" or "conventional' techniques. An adsorptive solid matrix is used in solid phase extraction and there are many studies about development of new, cheap, reusable adsorbents as solid phase extraction matrix. Liquid extraction is one of other alternative choice for sample pretreatment technique which allows the preconcentration and separation of analyte in a test tube. Among the extraction techniques, liquid liquid extraction is generally the simplest and most common one. The high consumption of organic solvents and secondary harmful residue are the main drawbacks of the conventional liquid liquid extraction. The newest alternatives to conventional extraction techniques are 'micro extraction' techniques. In these extractions, generally micro liters of organic phase is used and for formation of fine droplets of organic phase, disperser solvents generally are added.

The micro extraction techniques can be divided mainly into three classes, the first is conventional micro extraction in which the water immiscible conventional solvents like chloroform is used. The second one is cloud point, in which the nonionic surfactants generally used and a heating step is generally unavoidable in this technique. The third one is ionic liquid based micro extraction, in which generally room temperature ionic liquids are employed [23- 28]. The main advantage of ionic liquid micro extraction is low contact with the toxic organic vapor for the researcher. Besides, the consumption of ILs in micro liter range provides high enrichment factor. The most used ILs in extraction are consisted of asymmetric organic cations of pyridinium and imidazolium ring with alkyl groups attached and inorganic polyatomic anions such as PF_6^- and BF_4^- [29]. In conventional liquid liquid microextraction, hydrogen bonding, dipole dipole and van der Waals are the main interactions, in addition of these electrostatic repulsion and attraction are other interactions exists in IL based microextractions [29]. The low vapor pressure and low immiscibility of ionic liquid made scientist to focus on development of new simple and green extraction techniques with using these environmentally benign chemicals.

Due to widespread use of zirconium compounds in new medicinal and biological applications, development and validation of new simple analysis techniques are important. In the present study, we investigated a new spectrophotometric method for determination of zirconium. The method is based on the formation of zirconium-Br-PADAP complex and extraction of Zr-Br-PADAP complex into ionic liquid, 1-Hexyl-3-methylimidazolium hexafluorophosphate [C6MIM][PF6]. The cloudy behavior of solution which indication of dispersion of ionic liquid is simply achieved by addition of Triton X 114. The method is successfully applied to determination of zirconium in water, artificial saliva and dental materials. To the best of our knowledge, the combination of Br-PADAP and [C6MIM][PF6] has been used for first time for the separation, preconcentration and determination of zirconium.

Materials and methods

Reagents

All the chemicals are of analytical grade. They were purchased from Merck (Darmstad, Germany), Sigma Aldrich chemical company, and Carlo Erba Reagents. They were used without purification. The 1000 µg/L zirconium solution was prepared by dissolution of appropriate amount of ZrCl4 in 2.0 mL of 0.1 % nitric acid solution and solution was diluted to 100 mL with distilled water. The acetate buffer solutions were prepared from 1M of each acetic acid and sodium acetate. Br-PADAP solution was prepared as follows: 0.0060 g of Br-PADAP was dissolved in 10 mL of absolute ethanol and diluted to 25 mL with water. The solution was prepared daily. 1.0 % Triton X 114 solution was prepared by dissolution of 1 g of reagent in distilled water and diluted to 100 mL. 1-Hexyl-3-methylimidazolium hexafluorophosphate [C6MIM][PF6] was used as room temperature ionic liquid and used without purification.

The spectrometric measurements were conducted with a MAPADA series 6 spectrophotometers. The pH of solutions was adjusted with Sartorius basic pH meter. A Shimadzu analytical balance was used for weighing the reagents. A Biosan Bio RS-24 model multi rotator was used for effective mixing of the tubes.

Recommended spectrophotometric procedure for determination of zirconium

An aliquot of real sample or zirconium standard solution was mixed with 0.7 mL of Br-PADAP, after addition of 2 mL of pH 4.5 acetate buffer solution was mixed rigorously. 1 mL of 1% Triton X-114 was added and the solution was diluted to 14 mL with distilled water. The solution was incubated at room temperature for ten minutes to reach equilibrium, then 90 µL of ionic liquid [C6MIM][PF6] was added slowly and the solution became turbid. Solution was mixed with Biosan Bio RS-24 model multi rotator for 10 min. The efficient mixing of solution was done for complete transfer of Br-PADAP-Zr complex into IL phase. The solution was centrifugated for 20 min to separate the phases. After discharging the aqueous phase 500 µL of acetonitrile was introduced to sample and vortexed for 30 seconds to solubilize the ionic liquid phase. The spectrophotometric measurements were recorded with spectrophotometric quartz cell (volume: 500 µL) against reagent blank at 578 nm.

Total dissolution of zirconium based dental material with microwave digestion

For the dissolution of dental material, various concentrated acid and acid mixtures were tried. The total dissolution of material was achieved only the modified procedure given by Ma et al. [30]. The modified procedure was briefly as follows: 0.100 g of powdered dental material was mixed with 5 mL of concentrated H_2SO_4 and 2.500 g of $(NH_4)_2SO_4$. The digestion program was consisted of two stages: In the first, samples were digested for 10 min at 310 W and the second 20 min at 630 W. After cooling, the microwave tubes were opened carefully in a funnel and solutions were transferred to a graduated flask. The solutions were completely clear and diluted to 100 mL with distilled water. Blank samples were treated with same procedure without dental materials. The zirconium content was determined with proposed method.

Release of zirconium from dental material to artificial saliva

The zirconium release studies were conducted with a modified form of Fusayama's artificial saliva [31, 32], consisted of 0.081 g of $CaCl_2.2H_2O$, 0.078 g $NaH_2PO_4.2H_2O$, 0.043 g KCl, 0.04 g NaCl, 0.1 g urea, 1 mL of 0.05 % of $Na_2S.9H_2O$ in 100 mL of distilled water. The powdered and solid dental filling material was treated with artificial saliva for three days with continuous mixing via multi shaker system. The released amount of zirconium was determined with proposed method and recovery % values were found after spiking of exact amount of standard zirconium solution.

Results and discussion

In the present study, an ionic liquid based extractive and spectrophotometric determination of zirconium was proposed. The method is based on formation of zirconium Br-PADAP - complex in slightly acidic medium and preconcentration of complex into the ionic liquid phase (Fig. 1). As shown from Figure 1, a linear increment is achieved while the concentration of zirconium gradually increases. From this point of view, the linear absorbance response to Zr can be used for determination of the metal spectrophotometrically. In the method, the dispersion of IL into the aqueous solution is easily achieved by addition of non ionic surfactant, Triton X 114. To attain high sensitivity, accuracy and reproducibility, each experimental parameter (e.g. concentration of the reagents, volume of ionic liquid, centrifugation time, etc.) were optimized individually. Each parameter was optimized while the others were constant. Zr concentration was kept constant at 142 μg L^{-1} for the optimization of the parameters (e.g. Triton X 114, Br PADAP, IL). For pH optimization, in especially basic medium, the ΔA values were so close to zero while using 142 μg L^{-1} and the repeatability of the results were low, then 284 μg L^{-1} of Zr was used for this step. For all optimization studies, ΔA values were calculated from the absorbance difference of solutions with and without Zr.

The one of the most important factor that affects the formation of a complex for a given reaction may be the acidic or basic character of the solution. In most cases, the formation of a complex is directly related with the pH of experimental medium. Sometimes, the complex formation ability of certain species is less pH dependent. For both cases, e.g. the formation of complex strongly or not strongly dependent on pH of medium, the pH is generally the first parameter to be optimized. In the present study, acetate buffer was used to investigate the pH dependence of the formation of Br-PADAP-Zr complex.
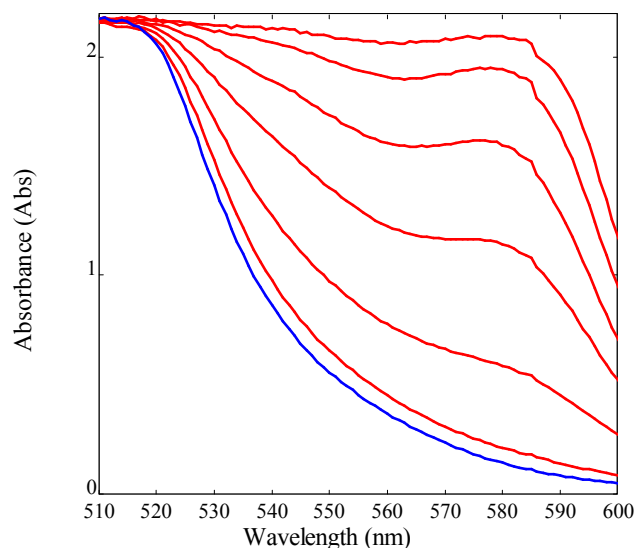

Figure 1. UV-vis. spectrum of Br-PADAP (in ionic liquid phase), blue line: in the absence of zirconium, and red lines: in the presence of zirconium (from bottom to top zirconium concentration increases: 36-714 μg L^{-1}).

The effect of pH was investigated in the range of 3.0-8.0. As shown from Figure 2, maximum absorbance difference was attained at the pH range of 4.0 to 4.6. Similar observations were found for other studies [33, 34]. A pH value of 4.5 was chosen for the further studies.

The effect of Br-PADAP concentration was studied in the range of 2.45×10^{-5}-1.23×10^{-4} M. As shown from Figure 3, a significant depression in ΔA was achieved as increasing the Br-PADAP. As Br-PADAP partially dissolves in water, the EtOH was used for total dissolution of the reagent. The ΔA value decreased with increasing the Br-PADAP concentration is mainly due to solubilisation of ionic phase because of high concentration of EtOH. The high solubility of ionic phase made the non-quantitative extraction of the complex. The 5.0×10^{-5} M Br-PADAP was chosen for further studies.
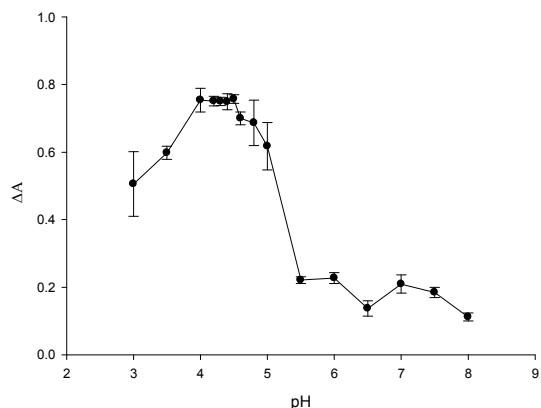
Figure 2. Effect of pH on preconcentration via ionic liquid microextraction and spectrophotometric determination of Zr

The migration of Br-PADAP-Zr complex into ionic liquid phase is a critical point of the proposed method. For effective (both quantitative and less time consuming) extraction, the dispersion of IL in aqueous phase is crucial. The dispersion of phase in the tiny droplet form should be achieved with a suitable way. Dispersion of organic phase with ultrasonic irradiation, strong vortexing or using dispersive agents is the most common method for this purpose. Among the stated ways, dispersion with non ionic surfactant is the simplest and economical one. Addition of small amount of surfactant generally accelerates the formation of small droplets. In the present study, Triton X 114 was used for the effective dispersion of the ionic liquid. Besides, it provides the anti sticking of IL to the test tube walls. Because of sticking of IL to test tube wall in the absence of surfactant, exact formation of phase in the bottom of tube was not achieved.
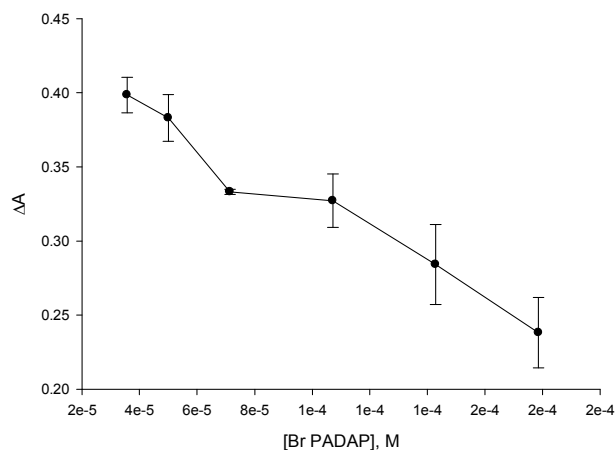

Figure 3. Effect of Br-PADAP concentration on preconcentration via ionic liquid microextraction and spectrophotometric determination of Zr
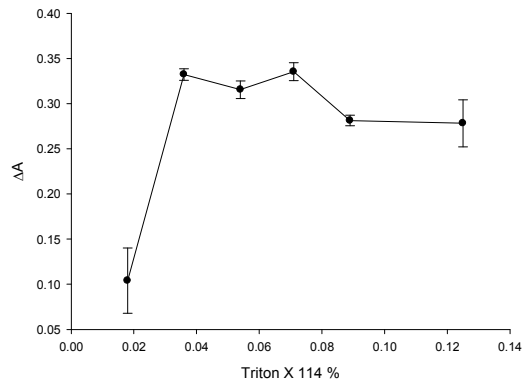

Figure 4. Effect of Triton X 114 concentration on preconcentration via ionic liquid micro extraction and spectrophotometric determination of Zr

The effect of Triton X 114 concentration was studied in the range of 0.018-0.125 %. As shown from Figure 4, absorbance difference of the system increased up to 0.071 % Triton X 114. From this point a significant depression was observed. The main reason of this behavior may be an increase in phase volume. This lead dilution of colored Br-PADAP zirconium complex phase. A concentration of 0.071 % triton X 114 was chosen for further studies.

[C6MIM][PF6] is an immiscible ionic liquid and can be used for liquid liquid micro extraction. The high solubility of organic compounds in ionic liquid phase makes ILs a good phase component of biphasic systems. The metal bonded organic compounds, e.g. Br-PADAP can be transfer to the ILs, so the quantitative extraction of analytes to micro liter IL can be achieved. In the present study, the effect of ionic liquid [C6MIM][PF6] was studied in the range of 0-120 µL. As shown from Figure 5, addition of IL causes significant increase in ΔA value. This is due to ability and tendency of Br-PADAP zirconium complex into non aqueous ionic liquid phase. A
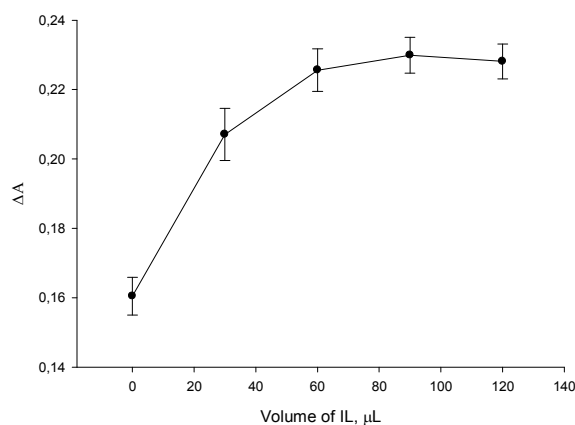

Figure 5. Effect of ionic liquid volume on preconcentration via ionic liquid micro extraction and spectrophotometric determination of Zr

significant increase in ΔA up to addition of 60 μL [C6MIM][PF6] was observed. The increase rate from 60 μL to 120 μL was not as notable as in the range of 0-60 μL. The high price of ionic liquids is one of important parameter that should be taken into consideration. The high price and sufficient ΔA made us continue the experiments with 90 μL.

Tolerance limits

The tolerance limits for some cations and anions were examined for proposed method (Table 1). The differentiation of absorbance was monitored as varying the concentration of possible coexisting ion. The maximum examined foreign ion/ zirconium ion ratio was 500. The tolerance limits were determined as the maximum ratio of ions that causes relative error equal or less than 5%.

Analytical figures of merit

The calibration curve of proposed method was linear in the range of 1.4-714 μg L^{-1} with a correlation coefficient of 0.99. Regression equation for calibration curve was found A=3.0C + 0.132 (A: Absorbance, C: Concentration). The LOD value of 3Sb/m was achieved as 0.012 μg L^{-1} (Table 2). The relative standard deviation (RSD) was found 5.7 %, 2.9 %, 2.3 % for ten replicate determinations of 0.036, 0.14, 0.29 μg mL^{-1}. The enhancement factor (EF, calculated from volume of sample solution divided by [C6MIM][PF6] volume) was found 156 for the proposed method. Recovery values of zirconium were found 98±2 at 95 % confidence level.

Application of the method to real samples

Application of a proposed method to real samples and successful results are the main expectation for method development. For this purpose, we applied the proposed method to dental materials and water samples. Dental material studies consisted of two parts, the first is about zirconium release to artificial saliva and the second is total microwave decomposition of dental filling material. As detailed mentioned in release of zirconium from dental material to artificial saliva section, dental material is contacted with artificial saliva and produced solution was analysed with proposed method. The added and found method was applied and the results can be seen in Table 3. As can be seen, the zirconium level in dental material conducted artificial saliva was below detection level for both solid and powdered material. Besides, the recovery values were lied between 95.5-111.7 %. The recovery values for water samples were also between 91.7-98.7 % for spiked samples. Microwave digestion of dental material results can also be seen from Table 3. The preliminary experiment showed us the solution obtained from direct microwave digestion contained too high amount of

zirconium, then the results were obtained after dilution of 100 μL of microwave digest to 100 mL. 500 μL of the resultant solution was analysed with the proposed method. The standard deviation results favor the reproducibility.

Comparison of proposed method with some existing literature studies

Because of its simplicity and low cost, research studies about spectrophotometric determinations of zirconium are highly abundant in the literature. But studies concerning the ionic liquid based extraction of Zr is highly limited. Beside, ionic liquids have been widely used for micro extraction of heavy metals and organic pollutants for various samples [46-48]. Some interesting examples are given in Table 4. From the table, it is obvious that the proposed method has comparable results and wide linear range. Enrichment factor of proposed method is rather high with compared to some of existing studies. The linear calibration range is also wide and it covers from ppt range to nearly ppm range. The applicability of proposed method to different matrix, e.g. artificial saliva, meets need for determination of Zr in such different matrix. Low consumption of organic solvents which are both harmful to environment and researchers is may be the most important superiority of the proposed method.

Conclusion

In the present study, an efficient separation, preconcentration and spectrophotometric determination of zirconium is proposed. The method is simple, low cost, sensitive, selective and green extraction technique. The analysis results have good accuracy, and precision. The consumption of organic solvent is highly limited and the method has a wide linear analytical calibration range. Our results can be comparable with literature values with respect to enhancement factor and detection limit. Low detection limit and high enhancement factor were observed in this study. The method is successfully applied to real samples, e.g. water, artificial saliva and dental materials.

Table 1. Tolerance limits for some possible coexisting ions

Possible coexisting ions	Foreign ion/ zirconium ion ratio
Na$^+$, K$^+$, CO$_3^{2-}$, HPO$_4^{2-}$, NO$_3^-$, CH$_3$COO$^-$	500
Ba^{2+}, Ca^{2+}, Mg^{2+},	125
Zn^{2+}, Ag$^+$	5
Ni^{2+}, Cu^{2+}, Fe^{3+}, F$^-$	<2

Table 2. Some analytic characteristics of proposed method

Calibration equation, r^2	A=3.0C + 0.132, r^2= 0.99
linear range	1.4-714 μg L^{-1}
limit of detection	3Sb/m=0.012 μg L^{-1}
[Br-PADAP]	5.0 x10^{-5} M
Triton x 114	0.071 %
pH	4.5 (prepared from 1 M acetic acid and 1 M sodium acetate)
Volume of (1-Hexyl-3-methylimidazolium hexafluorophosphate) [C6MIM][PF6]	90 μL
RSD (%)	5.7, 2.9 , 2.3 for determinations of 0.036, 0.14, 0.29 μg mL^{-1}
Enrichment factor	156

Table 3. Analysis results of real samples.

Sample ID	Added (μg/L)	Found (μg/L)	Recovery %
Artificial saliva I	-	BDL	-
(release from	143	143±6	99.9
solid filling)	285	291±13	102.0
Artificial saliva II	-	BDL	-
(release from	143	144±3	100.7
solid filling solid)	285	314±17	109.9
Artificial saliva III	-	BDL	-
(release from	143	136±11	95.5
powdered filling)	285	319±9	111.7
	-	23±0.8	-
Water Sample I	143	155±11	91.7
	285	305±16	98.7
	-	BDL	-
Water Sample II	143	140±6	97.5
	285	263±13	92.1

Microwave dissolution	Found (μg/mL)	Mean ±SD
Zr total dissolution I	242.4	
Zr total dissolution II	241.9	242.03±0.32
Zr total dissolution III	241.8	

RSC Advances

Table 4. Comparision of some existing literature with proposed method

| Remarks	Extraction medium (if exists)	Application	Analytical characteristics	References
The method is based on complex formation between promethazine and Zr-SCN complex in 1-3.5 M H_2SO_4.	$CHCl_3$	The promethazine method was applied to Zr in Zr steel.	6-204 ppm	[35]
The method is based on complex formation between zirconium and Methylxylenol Blue in weakly sulphuric acid solution	-		The curve was linear for 560 µg of zirconium in 25 ml solution.	[36]
The method based on complex formation between titanium zirconium and 2-hydroxy naphthaldehyde-p-hydroxybenzoic hydrozone	-	The method applied to steel samples.	0.456-4.56 µg/ml	[37]
The proposed method is based on the complex formation between uranium or zirconium with Alizarin Red S (ARS) and subsequent micelle-mediated extraction of products.	Triton X-114	The method was applied to determination of U and Zr simultaneously in water samples.	0.01-3 mg L^{-1} LOD: 0.8 µg L^{-1} EF: 20	[38]
The method based on a reaction between Demeclocyline (DMC) and Zirconium (IV)	-	-	0.91 to 7.35 µg/ml	[39]
Determination of trace amounts of vanadium(V) and zirconium(IV) in acetic acid medium using diacetylmonoxime salicyloylhydrazone	-	Standard alloy steel samples, mineral and soil samples.	Linear range 0.30-3.20 µg/mL for normal specta, 0.13–3.2 µg/mL for first order spectra LOD: 5.56×10^{-2} µg mL^{-1} normal specta LOD: 4.01×10^{-2} µg mL^{-1} for first order spectra	[40]
The method is based on the complex formation between arsenazo III and zirconium.	-	Aluminium alloy, magnesium alloy and copper alloy	-	[41]
Sequential extraction sheme: 1. zirconium into thenoyltrifluoroacetone (TTA) from about 4M HCl 2. Uranium (VI) into tri-n-octy lamine from about 4M HCl 3. Thorium TTA solution at pH about 1.5, and finally rare earths into TTA solution at pH about 4.7	Thenoyltrifluoroacetone and tri-n-octylamine	-	-	[42]
The method is based on complex formation between zirconium and Xipamide		Different real samples	0.2-3.6 µg/ml LOD: 0.041 µg/ml	[3]
Zr [IV] was sorbed in a dextran-type lipophilic gel as a complex with 2-(2-benzothiazolylazo)-3-hydroxyphenol.	Solid phase extraction	Water, soil, plant material and ore samples.	0.25-3.7 µg L^{-1} LOD: 150 ng L^{-1} (for 500 mL sample), 80 ng L^{-1} (for 1000 mL sample)	[1]
Zr was selectively extracted over Hf from sulfate medium by the amine-based extractants	Amin based extractants	-	The highest separation factor of 12.4 was obtained by using Alamine 308 from 0.5 M H_2SO_4 solution	[43]
Solvent extraction, separation of Zr and Hf by using LIX 63, PC 88A and mixture of PC 88A and LIX 63				[44]

using N-benzoyl-N-phenylhydroxylamine (BPHA) supported on a micro porous acrylic ester polymeric resin	Solid phase extraction	Sea water	LOD: 0.5 ppt and 99 % recovery for Zr	[45]
The method is based on complex formation between zirconium and Br-PADAP	1-Hexyl-3-methylimidazolium hexafluorophosphate	Water, artificial saliva and dental materials	1.4-714 µg L^{-1} LOD: 0.012 µg L^{-1} EF: 156	This study

Acknowledgment

References

1   A.S. Amin, *Journal of Taibah University for Science*, 2015, **9**, 227-236.

2   J.B. Ghasemi and E. Zolfonoun , *Talanta* 2010, **80**, 1191–1197.

3   A.S. Al-Kady , *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,*2012, **97**, 284–289

4   V. Sollazzo, F. Pezzetti, A. Scarano, A. Piattelli, C.A. Bignozzi, L. Massari, G. Brunelli and F. Carinci, *Dental Materials,* 2008, **24**, 357–361.

5   Y.K. Agrawal, M. Sanyal, P. Shrivastav and S.K. Menon, *Talanta*, 1998, **46**, 1041–1049.

6   B.A. Mckelvey and K.J. Orians, *Geochim. Cosmochim. Acta,* 1993, **57**, 3801–3805.

7   S. Poehle, K. Schmidt and A. Koschinsky, *Deep-Sea Research I*, 2015, **98**, 83–93.

8   M. Raso , P. Censi , and F. Saiano, *Talanta*, 2013, **116**, 1085–1090.

9   M. Afzal, J. Hanif, I. Hanif, R. Oadeer and M. Saleem, *J Radioanal. Nucl. Chem.,* 1990, **139**, 203-214.

10 H.A. Arida, *Talanta*, 2008, **76**, 40–43.

11 C. P. Zhang, D.Y. Qi and T.Z. Zhou, *Talanta*, 1982, **29**, 1119-1121.

12 A. Jain, O. Prakash and L.R. Kakkar, *J. Anal. Chem.*, 2010, **65**, 820–824.

13 S. A. Mohammed and H.H. Ahmad, *J. Raf. Sci*., 2009, **20**, 74-83.

14 G.V. Rathaiah and M.C. Eshwar, *Talanta*, 1988, **35**, 502-504.

15 S. Shibata, Y. Ishiguro, and T. Matsumae, *Anal. Chim Acta*, 1960, **23**, 384–387.

16 S.S. Goyal and J.P. Tandon, *Talanta*, 1968, **15**, 895–899.

17 A. Majeed and M.S. Khan, *Anal. Chim. Acta*, 1987, **192**, 125-128.

18 T. R. Dulski, *Talanta*, 1982, **29**, 467–471.

19 R.T. van Santen and J.H. Schlewitz, and C.H. Toy, *Anal Chim. Acta*, 1965, **33,** 593-596.

20 U.D. Uysal, A.A. Hüseyinli and T. Giray, *Journal of Scientific & Industrial Research*, 2011, **70**, 45-50.

21 S.G. Nagarkar and M.C. Eshwar, *Microchim. Acta*, 1974, **62**, 797-800.

22 S.Ganesh, P.Velavendan, N.K.Pandey, U.Kamachi Mudali and R.Natarajan, *International Journal of Advances in Chemistry (IJAC)*, 2014, **2**, 15-22.

23 E. M. Martinis, P. Berton and R.G. Wuilloud, *Trends Anal. Chem.*, 2014, **60**, 54-70.

24 S. Sadeghi, A.Z. Moghaggam, *RSC Adv.,* 2015, **5,** 60621-60629.

25 J. N. Sun, Y.P. Shi and J. Chen, *RSC Adv.,* 2015, **5,** 37682-37690.

26 H. Kang, X. Wang, Y. Zhang, J. Wu and H. Wang, *RSC Adv.,* 2015, **5**, 14631-14636.

27 S. Rastegarzadeh, N. Pourreza and A. Larki, *Ind. Eng. Chem.*, 2015, **24**, 297-301.

28 H.F. Wu, S. K. Kailasa, J.Y. Yan, C.C. Chin and Ku, H.Y. *J. Ind. Eng. Chem.*, 2014, **20**, 2071- 2076.

29 D. Han, B. Tang, Y.R. Lee and K.H. Row, *J. Sep. Sci.*, 2012, **35**, 2949-2961.

30 X. Ma and Y. Li, *Anal. Chim. Acta.*, 2001, **579**, 47-52.

31 D. Mareci , G. Bolat, A. Cailean, J.J. Santana, J. Izquierdo and R.M. Souto, *Corrosion Science,* 2014, **87**, 334–343.

32 T. Fusayama, T. Katayori and S. Nomoto, *J. Dent. Res.*, 1963, **42**, 1183-1197.

33 D. Afzali, F. Fathirad, S. Ghaseminezhad and Z. Afzali, *Environ Monit Assess,* 2014, **186**, 3523–3529.

34 S. Oszwaldowski, R. Lipka, T. Majewski and M. Jarosz, *Analyst*, 1998, **123**, 1529–1533.

35 P.G. Ramappa and S. Manjappa, *Current Science*, 1984, **53**, 630-1.

36 M. Deguchi and T. Kunishige, *Bunseki Kagaku*, 1972, **21**, 392-394.

37 G. Sumathi and T. S. Reddy, *International Journal of Chemical Studies,* 2014, **2**, 52-54.

38 J.B. Ghasemi, B. Hashemi, and M. Shamsipur, *Journal Of The Iranian Chemical Society(Jıcs)*, 2012, **9**, 257-262.

39 T. R. Kishore, T. R. Krishna and V. Suryanarayana Rao, *Der Chemica Sinica*, 2013, **4**, 194-197.

40 A. Varghese, I. *Spectrochimica acta, Part A, Molecular and biomolecular spectroscopy*, 2012, **95**, 46-52.

41 R. Ying, Y. Zhongxia, *Chinese Journal of Analytical Chemistry*, 1989, **17**, 1109-1112.

42 H. Onishi, K. Sekine, *Talanta*, 1972, **19**, 473-8.

43 L.Y. Wang, M.S. Lee, *Separation and Purification Technology*, 2015, **142**, 83–89.

44 L.Y. Wang, M.S. Lee, *Hydrometallurgy*, 2014, **150**, 153–160.

45 S. Sun, J. Li, *Microchemical Journal*, 2015, **119**, 102–107.

46 Z. Gao and X. Ma, *Anal Chim. Acta.,* 2011, **702**, 50-55.

47 M. Zeeb, M.R. Ganjali, and P. Norouzi, *Food Anal. Methods,* 2013, 6, 1398-1406.

48 X. Ma, M. Huang, Z. Li, and J. Wu, *J. Hazard. Mater.,* 2011, **194**, 24-29.
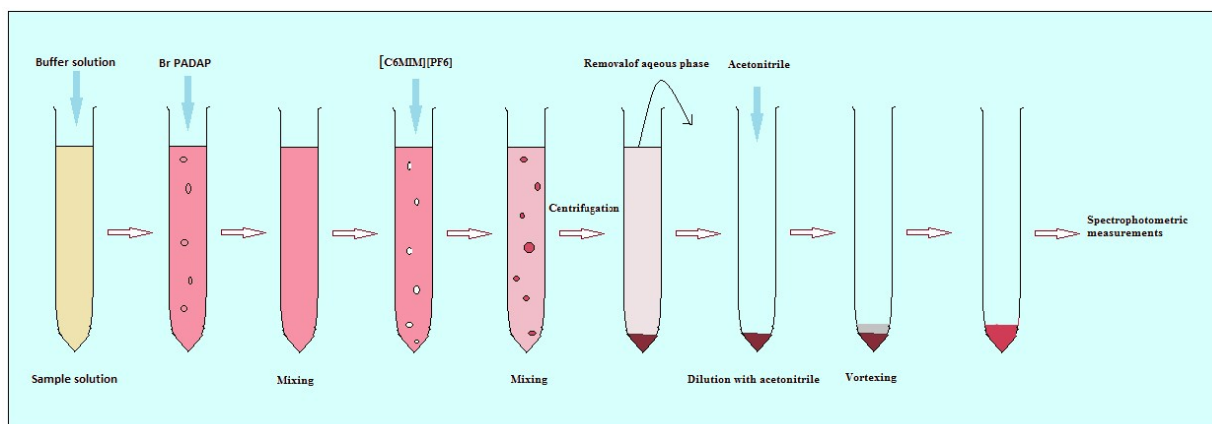
- A green extraction method was developed for the spectrophotometric determination of Zr.

- Proposed technique is simple, low cost, selective, sensitive and environmentally friendly.

- Br-PADAP and [C6MIM][PF6] was used as chelating reagent and extraction solution of Zr.

- High enhancement factor and low detection limit were achieved.

- Proposed method was applied to water, artificial saliva and dental materials