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Determination of Impurities in High Purity $ZrCl_4$ Material by ICP-MS after Separation of the Matrix using D2EHPA and ZrO_2 Nanostructure Product

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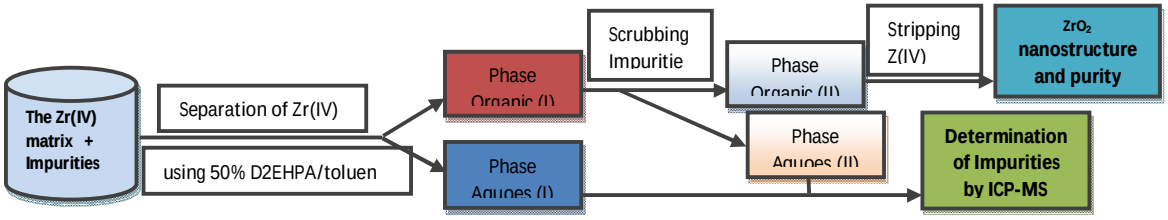
ABSTRACT

ICP-MS using matching matrix and internal standard is believed direct determination some impurities of high content in high purity $ZrCl_4$. However, trace impurities need to be separated from the Zr matrix to eliminate the interference of the matrix and determination of them by ICP-MS using the internal standard (as In, Bi). The study on capability extraction of Zr(IV) by di-2-ethylhexyl phosphoric acid (D2EHPA) were examined by infrared spectrum (IR) of $ZrO(NO_3)_2$ salt, D2EHPA-toluene solvent and Zr-D2EHPA-toluene complex. Impurities in $ZrCl_4$ were also determinate when using internal standard indium (In) after separation of them from the matrix Zr by extracting in 50% of dissolved D2EHPA in toluene. Investigation of separation of impurities from the matrix Zr showed that with using 50% D2EHPA/toluene solvent, after one cycle extraction using 3M HNO_3 and 1-2 cycles stripping Zr and scrubbing impurities by 6M HNO_3 can recovery for 95-100% of almost investigated impurity elements and stripping about 20-26% of Zr(IV) by ICP-MS using internal standard In. Our results indicated that with the mentioned amount of Zr, effect of the matrix Zr on the determination of almost elements by ICP-MS can be negligible. Levels of impurities were relative standard deviations (RSD) less than 8.4% and recovered (Rev) of 91.7-105.5%, so determination of impurities was high reliability and accuracy. After extraction of the Zr matrix in 3M HNO_3 and back-extraction by 1.5M H_2SO_4, stripping about 98,7% of the matrix Zr come back in aqueous phase and to get new ZrO_2 product. The energy dispersive X-ray (EDX) of new ZrO_2 product showed that it is purity. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed that the crystal structure and morphology of new ZrO_2 product are spherical and nanostructure, which can be applied on the treatment of metal ions in wastewater sources and anti-corrosion steel.

Graphical Abstract



Highlights:

- Separation impurities from the Zr(IV) matrix by solvent extraction using D2EHPA/toluene.
- Determination of impurities after separation by ICP-MS.
- Purity ZrO_2 nanostructure and apply on wastewaters or anti-corrosion steel.

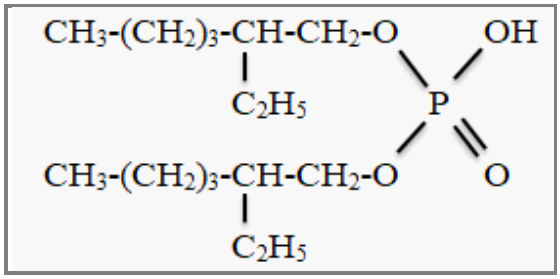
Keywords: Impurities, $ZrCl_4$, Extraction, D2EHPA, ICP-MS, ZrO_2 Nanostructure.

INTRODUCTION

Recently, many countries in the world have and will use nuclear power to replace other sources of energy. Zirconium materials with the high purity used as the fuel elements, reactor cans and pressure tubes for nuclear reactors because zirconium (Zr) is a excellent corrosion resistant material with a low neutron absorption cross-section (0.18 barn) **[1-4, 12]**. Some materials Zr (metal, oxide, alloys) have very high purity, but we still have many elements with different levels [**1-4**]. The presence of impurities will damage the precious properties Zr - that is, transparency with thermal neutrons affect on the properties of the material and the efficiency of a nuclear reactor, so that the specifications of the alloys must be strictly controlled. It is important to pay attention to products that high neutron absorption cross-section such as Hf, B, Cd, Gd, Sm [**1**]. Therefore, it is necessary to analyze impurities in high purity Zr materials to test and to evaluate before they are used in nuclear reactors.

One in modern analytical methods, namely as inductively coupled plasma mass spectrometry (ICP-MS) has the advantages of high sensitivity, low spectral interference and low matrix effects. Some investigations used ICP-MS for determination of impurities in Zr materials (ZrO_2, Zircaloy 360a, $ZrCl_4$) as showed in [**7-10**]. Several authors combined the separation of the matrix Zr by solvent extraction and determination of impurities after separation of the matrix by ICP-MS. They may be direct determination of impurities with high content by ICP-MS using matching matrix and internal standard indium (In). However, trace impurities need to be separated from the matrix to eliminate the interference of the matrix and determination of them by ICP-MS using the internal standard In. Solvent extraction has been regarded as one of the most promising operation to separation of the Zr(IV) matrix from metallic elements due to its great technical ease of carrying out the continuous mode.

Liquid-liquid extraction (or solvent extraction) is usually used to separate the Zr matrix from other elements by the same number of effective extractants as D2EHPA, Cyanex 272, PC88A, TBP [**10-18**]. A close search of literature indicates that the use of di-2-ethylhexylphosphoric acid (D2EHPA) as an Extractant for the solvent extraction of Zr(IV) from acid solutions were scarce [**11, 16, 17**]. D2EHPA is a new acid extractant (pK_a = 3.22 in methanol), molecular formula is $C_{16}H_{35}PO_4$ (M = 322.43 g mol^{-1}), with structural formula as follows:



In previous article, the author focused on separating of the matrix zirconium from other impurities by solvent extraction using solvents includes 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester

(PC88A) in kerosene that shows a great results for the determination of impurities in high purity $ZrCl_4$ [**18**].

In general, nanoscale materials and ZrO_2 nanoparticles have been explored for the treatment of PO_4^{3-}, F^-, Cr^{3+}, Cr(VI) ions in waste water and are results as good [**19-28**]. In addition, ZrO_2 nanoparticles and ZrO_2 nanoparticles/silane were fabricated on the surface of steel, increasing the adhesion between the steel surface and the coating, increasing the corrosion resistance of the steel to 2-3 times [**20, 21, 25**].

Although D2EHPA has been known long time ago as an extractant for trace amounts of Zr(IV) [**11**], its application for removing Zr matrix from a dissolved $ZrCl_4$ sample was not studied. So, investigation of determination of many impurities in high purity $ZrCl_4$ material after separation of the Zr matrix from nitrate using solvent extraction with D2EHPA dissolved in toluene by ICP-MS has been done. In addition, initial evaluation of ZrO_2 nanoparticle has potential for the application for treatment of heavy metal ions in water and corrosion resistant steel.

MATERIALS AND METHODS

Chemicals, materials and instruments: D2EHPA (di-2-ethylhexylphosphoric acid, 96.8%, Merck, Germany) and toluene were used as an extractant and diluent, respectively. $ZrOCl_2.8H_2O$ (Merck, 98%) was used as a source of Zr(IV). All other reagents were analytical reagent grade of Merck company, Germany as: $ZrCl_4$ powder, Zr(IV), Hf(IV), Ti(IV) standard solutions (1000 µg/mL) and multi element standard solution of 43 elements (include Ag, Al, B, Bi, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn, Sc, Y, U, Th, 14 rare earth elements) 1000 µg mL^{-1}; Super pure HNO_3, $HClO_4$ and ultra water 18 MΩ.

The IR spectrum of salt, solvent and complex was recorded using FT/IR (Affinity - 1S, Shimadzu, Japan). The concentrations of zirconium and other elements in the aqueous phases were determined by ICP-MS (Agilent 7500a, USA) instrument, other apparatus such as separators and shaker were used in the study. For characterization of the produced ZrO_2 was done using number of techniques. Energy dispersive X-ray spectroscopy (EDX, Modul ISIS 300 Oxford England) was determined level of elements. The X-ray diffraction (XRD) patterns of the product was collected at room temperature using a D8 Advance (Germany) with $CuK_{\alpha 1}$ - λ = 0,154056 nm radiation. The morphology was studied using transmission electron microscopy (TEM). TEM images were obtained using a JEOL JEM-1010 TEM operating at 80 kV. Samples for TEM imaging were prepared by suspending a former carbon-coated, 300 mesh copper grid (Ted Pella) in ethanol-diluted samples for approximately 2 min.

Analytic methods for separation of Zr(IV) and determination of impurities:

Dissolution procedure: The $ZrCl_4$ powder was weighted of 1.9204 gram, then dissolved in 5 mL of nitric acid concentrates and boiled until the solution turned from yellow to colorless. Heating the slowly, dissolved and added up to the mark 25 mL by 0.3M and 3M HNO_3. The concentration of Zr(IV) in these solutions is 30 mg mL^{-1}.

Separation of Zr(IV) from HNO_3 media by D2EHPA/toluene solvent: Aqueous phase containing 30 mg mL^{-1} Zr(IV) and other impurities in 3M HNO_3 media. Organic phase was 50% D2EHPA in toluene. Equal volumes of aqueous phase and organic phase were contacted for 60 min with a mechanical shaker, equilibrated 30 min at room temperature (25±0.5^{0}C) unless stated otherwise. Separated aqueous phase and stripping of elements in organic phase from 1 to 2 cycles by 6M HNO_3 solutions. Merged aqueous phase and stripping solutions, added 5 mL of (25% HNO_3+ 20% $HClO_4$) solutions, evaporated to dryness, added internal standard In and dissolved in 0.3M HNO_3 solutions to volume of 10 mL for measuring on ICP-MS (Agilent 7500a) to determine of impurities.

Characterization of ZrO_2 product after solvent extraction using D2EHPA/toluene: Fixed volume of the aqueous phase (1.5M H_2SO_4) were contacted for 60 min with different volumes of the loaded D2EHPA until equilibrium is obtained keeping fixed phase ratio (A:O) 1:1. A measured portion of the aqueous phase was taken for zirconium analysis. After stripping process, the stripping agent loaded with zirconium was adjusted by ammonia solution to pH = 9 to precipitate zirconium as $Zr(OH)_4$ which filtrated and dried at 60°C overnight, then burned at 600°C for 5 hours to form ZrO_2 which used for complete characterization.

RESULTS AND DISCUSSION

Operating parameters used for determination of elements by ICP-MS Agilent 7500a: We choose the mass number of analytical elements based on the principle that the mass number chosen is the isotope having the greatest abundance and not the same ratio of m/z to the isotope of the other elements. If the coincidence occurs, select another isotope with less common. An inductively coupled plasma mass spectrometer (ICP-MS Agilent 7500a, USA) was employed in the present work. The applied ICP-MS optimum operating parameters are summarized in table 1.

Table 1. Operating parameters used for studying the concentrations of elements by ICP-MS Agilent 7500a.

ICP operating conditions	
Radio frequency power	1200W
Plasma gas flow rate	15 L min^{-1}
Carrier gas flow rate	1.2 L min^{-1}
Auxiliary gas flow rate	0.9 L min^{-1}
Peripump rate	0.4 rps
Time pump (uptake)	90s
Pump speed stability	0.1rps
Stable injection time (stable)	30s
Coolant	2.4 L min^{-1}
Temperature spray chamber (S/C) and coolant	20^0 and 17^0C
Nebulizer	Cross flow nebulizer
ICP-MS interface	
Sampling cone	Nickel with 1.0 mm orifice
Skimmer cone	Nickel with 0.75 mm orifice
ICP on pressure	7.3 x 10^{-3} Pa
Scanning (peak hopping)	
The pulse level and the ion of lens	1000 V and 5.75V
Mass resolution (m/Δm)	300
Mass range of scan	3 - 240 u
Measurement time for one point	0.1s
Number of repeat measurements	3
Points per peak	3

The matrix effects of Zr were investigated and most of the spectral interferences were avoided by using internal standard element. In and as the internal standard was used to eliminate the interference of the matrix for determination of impurities in $ZrCl_4$. Since the matrix effects of a high Zr concentration on the peaks of the internal standard were similar to those on almost all of the analytic elements. The internal standard method was quantitative analysis.

The direct determinations (with matching matrix and internal standard method) by ICP-MS for 14 impurities (Al, Si, Ti, V, Cr, Fe, Ni, Zn, Nb, Mo, Sn, Ta and W) in high purity $ZrCl_4$ powders have the values RSD <8.4% and Rev from 93.2 to 103.4%. The Student standard test shows that the direct determination results are high accuracy and well-matched to the certified values of high purity zirconium materials and previous article [2-4, 18].

IR spectral studies of $ZrO(NO_3)_2$ salt, D2EHPA-toluene solvent and the extracted complex Zr-D2EHPA-toluene: The study on capability extraction of Zr(IV) by D2EHPA were examined by infrared spectrum (IR) of $ZrO(NO_3)_2$, D2EHPA-toluene and Zr-HNO_3-D2EHPA-toluene. IR of the salt, solvent and the extracted complex showed on figure 1.

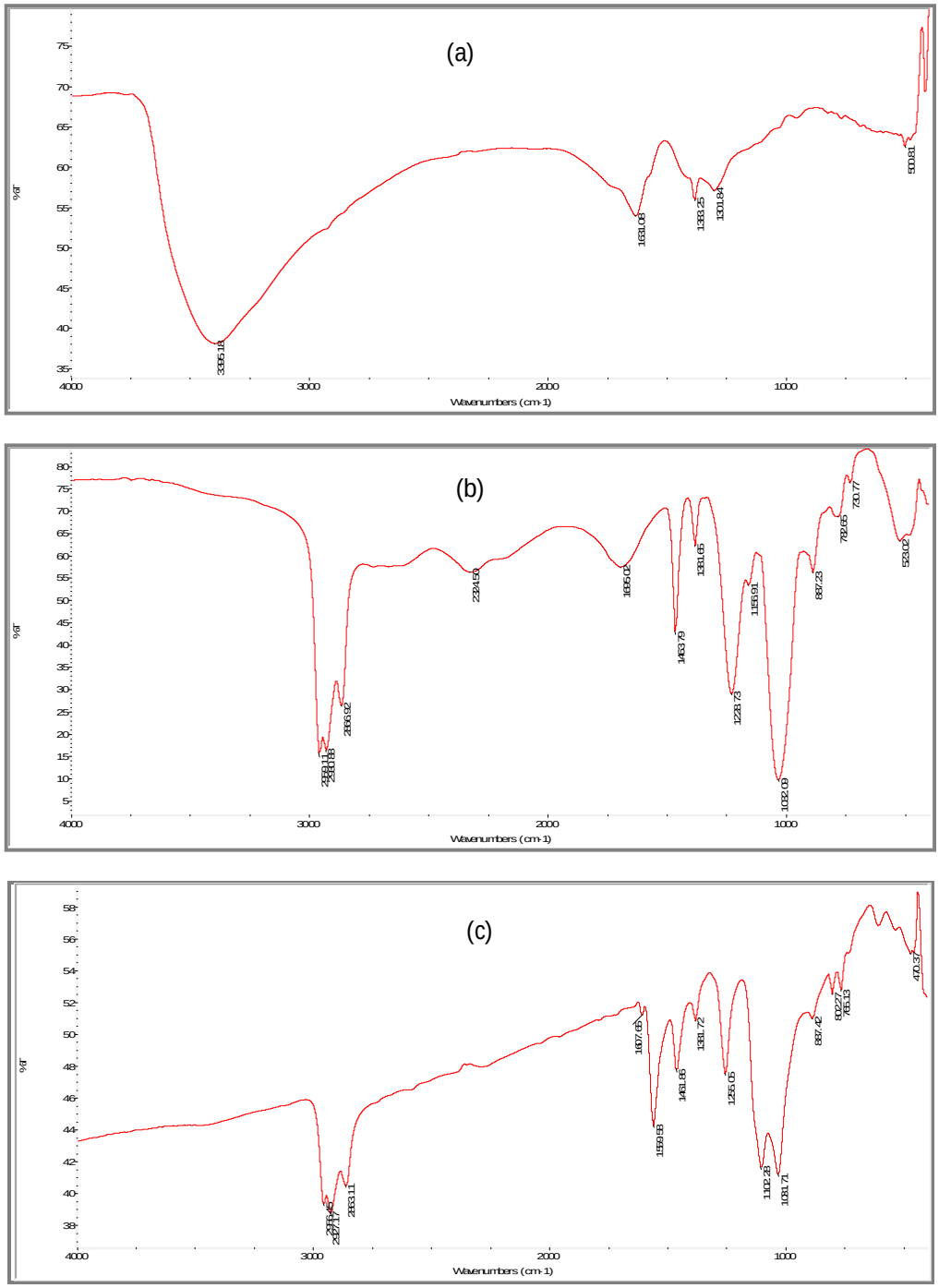


Figure 1. Infrared spectrum of Zr(IV) (a), D2EHPA-toluene (b) and Zr-HNO_3-D2EHPA-toluene (c).

The infrared spectra of $ZrO(NO_3)_2$, D2EHPA-toluene and Zr-D2EHPA-toluene complex were recorded. The infrared band at 1631.08 cm^{-1} for NO_3^- in $ZrO(NO_3)_2$ is transfer bands at 1559.58 cm^{-1} in

the complex. Moreover, the infrared band at 1032.09 cm^{-1} for P=O vibration in D2EHPA is split into two bands at 1031.71 and 1102.8 cm^{-1} in the complex indicating that both ions of the ion pair are probably have created strong bonds. In other words, there was coordinated of phosphoryl oxygen atom and Zr(IV) and NO_3^-. This result shows that there is strong complexity between D2EHPA and Zr(IV) in HNO_3 media. This result is consistent with the previous study [**6, 11, 18**].

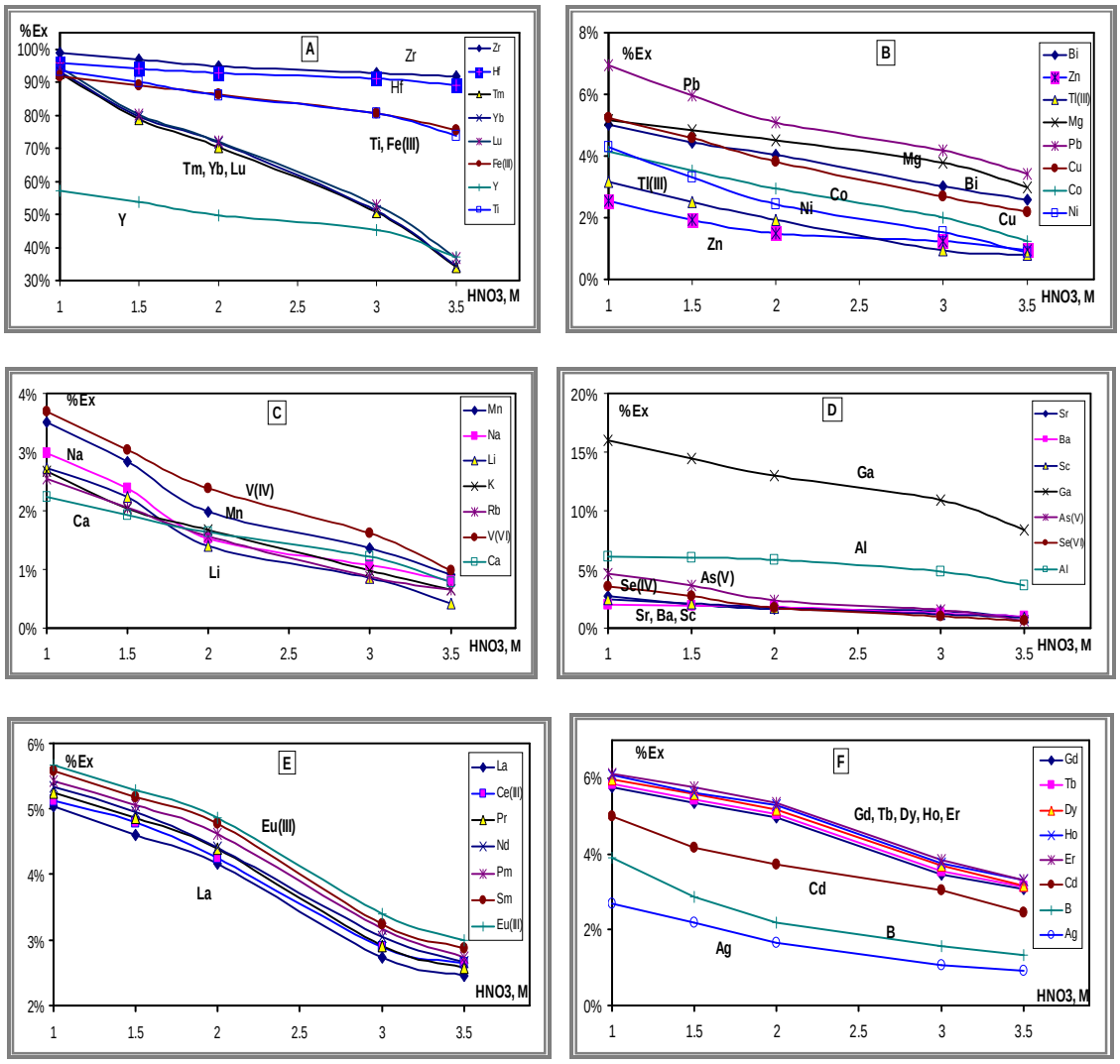


Figure.2. Effects of (1-3.5M) HNO_3 concentrations on the extraction efficiency of Zr(IV) and other elements with 50% D2EHPA/toluene solvent.

A-the extraction efficiency of Zr, Hf, Tm, Yb, Lu, Fe,Y, Ti B-the extraction efficiency of Bi, Zn, Tl, Mg, Pb, Cu, Co, Ni
C-the extraction efficiency of Mn, Na, Li, K, Rb, V, Ca D-the extraction efficiency of Sr, Ba, Sc, Ga, As, Se, Al
E-the extraction efficiency of La, Ce,Pr, Nd,Pm, Sm, Eu F-the extraction efficiency of Gd, Tb, Dy, Ho, Er, Cd, B, Ag

The effects of HNO_3 concentration on extraction procedure by using 50% D2EHPA/toluene solvent: Effects of (1-3.5M) HNO_3 on the extraction efficiency of Zr(IV) and other elements show on figure 2. Figure 2 shows that when increasing HNO_3 concentration, the extraction efficiencies of Zr(IV), Hf(IV) were very high (from 89 to 99%) and reaching stable. Some elements were highly extracted such as Fe(III), Y, Tm, Yb and Lu whereas the extraction efficiencies of other elements were decreased. The extraction efficiency of Zr(IV), Hf(IV) was 93%, 91%, respectively, Y, Tm, Yb and Lu

of 45-53%, Fe of 80.5%, Ga of 11% and extraction efficiencies of other elements were less than 5% with 3M HNO_3. The extraction efficiency of almost REEs was low (from 2.72 to 3.74%).

From stripping results of Zr(IV) in the section (stripping of zirconium from loaded D2EHPA/toluene), we chose 6M HNO_3 solutions for 1 to 2 cycles stripping of impurities after extraction process containing of 30 mg mL^{-1} Zr and 0.5 µg L^{-1} of each impurity from 3M HNO_3. The analytic results of elements by ICP-MS in aqueous phase and organic phase were investigated in table 2 and table 3.

Table 2. Contents of elements in aqueous phase and organic phase after 1 extraction by 3M HNO_3 and 1 stripping by 6M HNO_3 with 50% D2EHPA/toluene.

Elements	Li, B, Na, K, Rb, Mg, Ca, Sr, Ba, Al, Ga, Tl, Sc, Cd, Ag, Bi, Zn, Pb, Cu, Co, Ni, Mn, V, As, Se, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er	Tm, Yb, Lu	Y	Ti, Fe	Hf	Zr
Aqueous phase,%	≈100	85-87	91	58	25	20
Organic phase,%	Not detected	13-15	09	42	75	80

Table 3. Contented of elements in aqueous phase and organic phase after 1 extraction by 3M HNO_3 and 2 cycles stripping by 6M HNO_3 with 50% D2EHPA/toluene.

Elements	Li, B, Na, K, Rb, Mg, Ca, Sr, Ba, Al, Ga, Tl, Sc, Cd, Ag, Bi, Zn, Pb, Cu, Co, Ni, Mn, V, As, Se, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er	Tm, Yb, Lu	Y	Ti, Fe	Hf	Zr
Aqueous phase, %	≈ 100	95-96	96	65	32	26
Organic phase, %	Not detected	04-06	04	35	68	74

Tables 2 and 3 were detected after 1 extraction by 3M and 1 to 2 cycles stripping by 6M HNO_3 solutions, the recoveries were found as 95-100% so that 41 elements could separated and Zr remained in water phase about 20-26%. It was found that with the mentioned amount of Zr, effect of Zr on the determination of elements except Hf, Ti, Fe by ICP-MS can be negligible. This extraction system can be used for determination of impurities in materials of nuclear grade and high purity zirconium by ICP-MS.

Stripping of zirconium from loaded D2EHPA/toluene: All the experiments were performed on the pregnant organic solution D2EHPA, a mixture of 10 mL of the loaded organic (29.98 mg mL^{-1} of Zr(IV) and certain volume of stripping agent (keeping the required phase ratio) was stirred vigorously in 60 mL beaker using magnetic stirrer and at room temperature for certain contact time. The mixture then transferred to a separating funnel and allowed to be settled down for 30 min. The aqueous and organic phases were separated and the aqueous samples were analyzed. Results of stripping of zirconium from loaded D2EHPA/toluene with 20 extraction solutions are shown in table 4.

As shown in table 4, stripping of zirconium from loaded 50%D2EHPA/toluene has been carried out using H_2SO_4 as the most effective stripping agent. The feasibility of using D2EHPA for separation of zirconium was assisted by stripping studies. The loaded zirconium onto D2EHPA/toluene has been stripped with stripping efficiency 98.7% when using 1.5M H_2SO_4 as an efficient eluting agent at 60 min contact time and phase ratio O:A (v:v) as 1:1.

Determination of other impurities in high purity $ZrCl_4$ by ICP-MS after separation of the matrix: Solvent of 50% D2EHPA/toluene was used to removal of the matrix Zr from 3M HNO_3 solutions, and then washed extraction of the organic phase 2 cycles by 6M HNO_3 solutions. Determination of other impurities by ICP-MS after separation of the matrix (with the standard addition method and internal standard of 150 µg L^{-1}) in high purity $ZrCl_4$ (repeat 3 times) was showed in table 5.

Table 5 shows that the levels of impurities in $ZrCl_4$ from 0.071 µg g^{-1} (Lu) to 23.876 µg g^{-1} (Ba). Thus, from the standard of purity nuclear, the $ZrCl_4$ material was purity analysis. On the other hand, the

results of the determination of impurities after separation of the matrix Zr by ICP-MS have the recovery percentage from 91.7 to 105.5% for different impurities. The %RSD of the methods varying between 2.5 and 5.7% for a set of three (n = 3) replicates was found for the $ZrCl_4$ material and the certification reference sample (zircaloy 360b). Determination of trace impurities in high pure zirconium samples (Merck) was performed. $ZrCl_4$ material is highly pure (>99.6%) and analyzed successfully without spectral interference and the high reliability determination of impurities. The student standard test shows that after separation of the matrix zirconium, the determination results are high accuracy and well-matched to the certified values of high purity zirconium materials [1-4].

Table 4. Stripping efficiency (%) of Zr(IV) from loaded 50%D2EHPA/toluene with some extraction solutions.

S.No.	extraction solutions	Stripping efficiency (%)	S.No.	extraction solutions	Stripping efficiency (%)
1	1M HCl	20.5	11	6M HNO_3	6.0
2	2M HCl	26.0	12	8M HNO_3	11.5
3	3M HCl	27.5	13	1M HCl + 1% H_2O_2	25.0
4	4M HCl	28.0	14	2M HCl + 1% H_2O_2	41.0
5	0.5M H_2SO_4	94.5	15	1M HCl + 2% H_2O_2	35.0
6	0.7M H_2SO_4	95.0	16	2M HCl + 2% H_2O_2	48.0
7	1M H_2SO_4	98.5	17	2M HNO_3 + 1% H_2O_2	5.5
8	1.5M H_2SO_4	98.7	18	4M HNO_3 + 1% H_2O_2	6.5
9	2M HNO_3	3.0	19	2M HNO_3 + 2% H_2O_2	6.0
10	4M HNO_3	4.5	20	4M HNO_3 + 2% H_2O_2	13.0

The procedure proposition has advantages over other pre-concentration techniques because it does not require any specific reagents and/or conditions for various elements. It is also superior with respect to the efficiency and applicability to a large number of metallic ions, specifically the transitional elements and rare earth elements commonly associated with zirconium. This work will be applied to the determination of impurities in zirconium materials of high purity manufactured by Merck and NIST namely as ZrO_2, $ZrO(NO_3)_2$, $ZrOCl_2$, Zircaloy-2, Zircaloy-4, Zircaloy 360a.

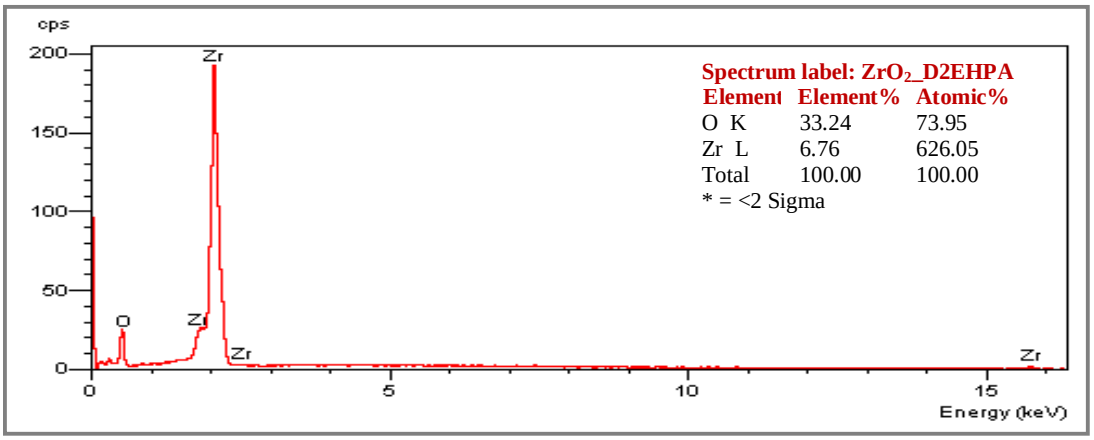


Figure 3. The EDX of ZrO_2 product after solvent extraction by D2EHPA/toluene.

Characterization of ZrO_2 product: The EDX, XRD and TEM of ZrO_2 product show on figures 3, 4 and 5 [22-28]. Figure3 indicate that the EDX for zirconia sample shows the main components of ZrO_2 are Zr (66.76%) and O (33.34%), with a total content of nearly 100%. This shows that the ZrO_2 product after purification by solvent extraction with D2EHPA/toluene has very high purity. This is consistent with the levels of impurities (in table 5).

As shown in figure 4, the X-ray diffraction for zirconia sample shows the presence of diagonal phase (t) of zirconium oxide as the major with JCPDS (00-036-0420 and 00-050-1089 with two characteristic peaks of the d=3.161 and d=2.952) facets at 2θ°=28.203 and 30.240 respectively. The particle size of the formed zirconia from solvent extraction using D2EHPA was arranged between 24.55 and 24.76 nm this because D2EHPA in these experiments acts as extractor for zirconium and surfactant for the preparation of zirconium nanoparticles.

Table 5. Levels of impurities in high purity $ZrCl_4$ after separation of the Zr matrix by 50% D2EHPA/toluene.

Impurities	Levels (µg g^{-1})	RSD (%)	Added (µg g^{-1})	Total (µg g^{-1})	Rev (%)
Li	13.096±0.498	3.8	5.0	17.921	96.5
B	15.238±0.472	3.1	5.0	19.988	95.0
Na	5.553±0.216	3.9	2.5	8.016	98.5
Mg	0.814±0.027	3.3	2.5	3.339	101.0
K	13.300±0.752	5.7	5.0	18.525	104.5
Ca	2.369±0.101	4.3	2.5	4.969	104.0
Sc	1.006±0.039	3.9	2.5	3.416	96.4
Mn	6.839±0.265	3.9	2.5	9.302	98.5
Co	1.704±0.043	2.5	2.5	1.960	102.5
Cu	9.127±0.316	3.5	5.0	14.377	105.0
Ga	3.083±0.089	2.9	2.5	5.503	96.8
As	7.346±0.217	3.0	2.5	9.639	91.7
Se	0.284±0.009	3.2	2.5	2.597	92.5
Sr	18.646±0.600	3.2	5.0	23.416	95.4
Y	0.193±0.006	3.1	2.5	2.593	96.0
Mo	16.567±0.423	2.6	5.0	21.367	96.0
Ag	9.561±0.286	3.0	5.0	14.711	103.0
Cd	2.110±0.062	2.9	5.0	7.184	101.5
Ba	23.876±0.729	3.1	5.0	28.726	97.0
La	4.337±0.221	5.1	2.5	6.737	96.0
Ce	4.130±0.235	5.7	2.5	6.655	101.0
Pr	2.820±0.089	3.2	5.0	8.020	104.0
Nd	1.451±0.046	3.2	2.5	3.851	96.0
Sm	1.135±0.034	3.0	2.5	3.710	103.0
Eu	0.660±0.036	5.5	2.5, 5.0	3.185, 5.760	101.0, 102.0
Gd	0.096±0.004	4.2	2.5, 5.0	2.461, 4.846	94.6, 95.0
Tb	0.129±0.005	3.9	2.5, 5.0	2.517, 4.929	95.5, 96.0
Dy	0.143±0.006	4.2	2.5, 5.0	2.743, 5.418	104.0, 105.5
Ho	0.157±0.007	4.5	2.5, 5.0	2.732, 5.357	103.0, 104.0
Er	0.322±0.009	2.8	2.5, 5.0	2.685, 5.072	94.5, 95.0
Tm	0.136±0.006	4.4	2.5, 5.0	2.636, 5.186	100.0, 101.0
Yb	0.147±0.005	3.4	2.5, 5.0	2.722, 5.372	103.0, 104.5
Lu	0.071±0.004	5.6	2.5, 5.0	2.434, 4.846	94.5, 95.5
Tl	1.153±0.040	3.5	5.0	5.938	95.7
Bi	0.547±0.031	5.7	5.0	5.347	96.0
Th	0.265±0.012	4.5	2.5, 5.0	2.653, 5.080	95.5, 96.3
U	0.332±0.016	4.8	2.5, 5.0	2.717, 5.117	95.4, 95.7

Figure 5 indicate that the TEM for zirconia sample shows the particles obtained are spherical form, fairly uniformly distributed and have an average crystal size of ≤25nm. The results of TEM images of particle size are quite consistent with the XRD spectra. The results of the use of ZrO_2 nanoparticles as materials for treating metal ions in wastewater and fabricating the coatings prior to coating are reported in subsequent studies.

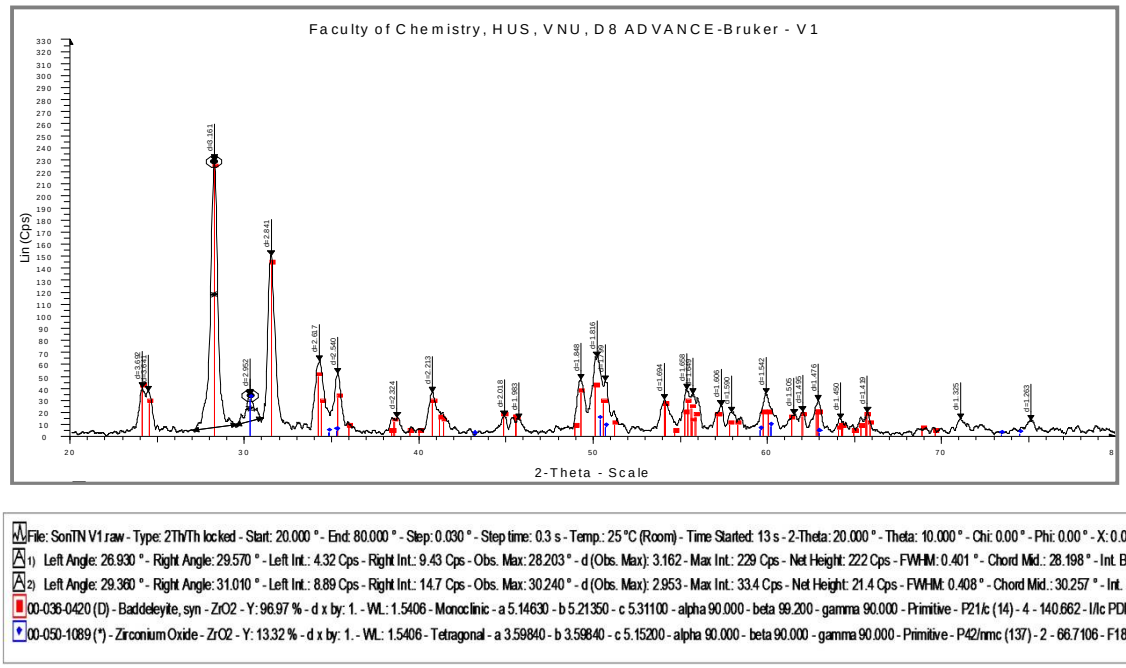


Figure 4. The XRD of ZrO_2 product after solvent extraction by D2EHPA/toluene.

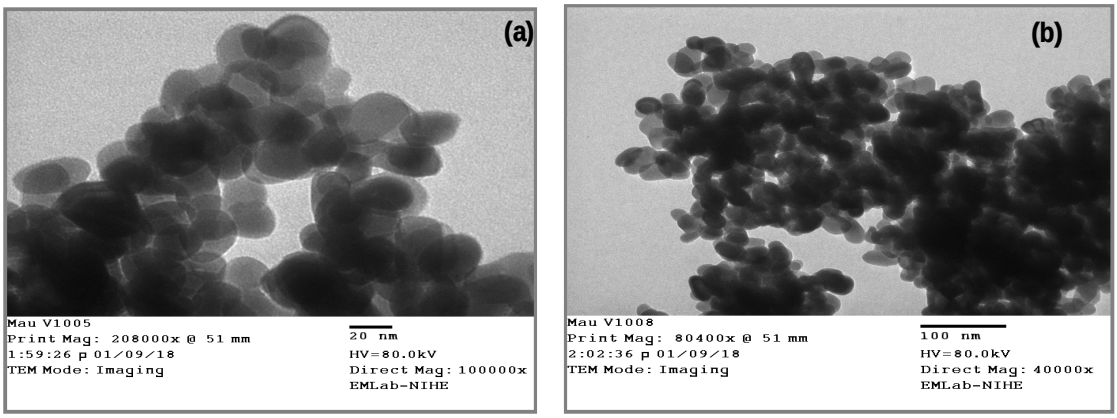


Figure 5. The TEM of ZrO_2 product after solvent extraction by D2EHPA/toluen (a-20 nm; b-100nm)

APPLICATION

Establishing method determination of impurities by ICP-MS in high purity and nuclear purity zirconium materials, which are used in nuclear reactors. The synthesized zirconium oxide nanoparticles will be used on the treatment of metal ions in wastewater sources and anti-corrosion steel.

CONCLUSIONS

Capability strong extraction of Zr(IV) by D2EHPA were examined by IR spectra of $ZrO(NO_3)_2$, D2EHPA-toluene and Zr-HNO_3-D2EHPA-toluene. When extraction systems containing of 30 mg mL^{-1} Zr(IV) and 0.5 µg L^{-1} of each impurity by 50% D2EHPA diluents in toluene, after 1 extraction from 3M HNO_3 and 1-2 cycles stripping by 6M HNO_3, more than 95% of almost elements could be separated

and Zr remaining in water phase is about 20-26%. It was found that with the mentioned amount of Zr, the effect of Zr on the determination of elements by ICP-MS can be negligible. Extraction systems with D2EHPA could be used for determination of impurities in materials of nuclear grade and high purity zirconium by ICP-MS. Determinable impurities results after separation of the matrix Zr by 50% D2EHPA/toluene (using standard addition and internal standard In) in high purity $ZrCl_4$ powders by ICP-MS. The values of RSD were less than 8.4% and Rev of 91.7 to 105.5%. After extraction and back-extraction was stripping about 98.7% of the matrix Zr come back in aqueous phase and to get new ZrO_2 product. The EDX showed that ZrO_2 product was very high purity. The XRD and TEM showed that the crystal structure and morphology of new ZrO_2 product are spherical and nanostructure, which can be applied on the treatment of metal ions in wastewater sources and anti-corrosion steel.

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