Nano ZrO$_2$ Synthesis by Extraction of Zr(IV) from ZrO(NO$_3$)$_2$ by PC88A, and Determination of Extraction Impurities by ICP-MS

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Abstract: High purity Zirconium (Zr) materials are essential in many components of nuclear reactors, especially fuel cladding tubes. Due to the matrix influence, determination of impurities in the Zr materials requires separation from the Zr matrix. Among extraction methods, solvent extraction is common and suitable for large-scale production. In this study, extraction capability of Zr(IV) by 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC88A) was examined by FT-IR and UV of ZrO(NO$_3$)$_2$ salt, PC88A-toluene solvent, and Zr-PC88A-toluene complex. ZrO$_2$ (obtained from Institute for Technology of Radioactive and Rare Elements—ITRRE), after being separated from the Zr matrix, was determined for impurities using internal standard (indium, In) by 50% of PC88A dissolved in toluene. Separation of impurities from the Zr matrix underwent two stages. First, one cycle of extraction of the Zr matrix and impurities in 3 M HNO$_3$ using 50% PC88A/toluene was conducted. Second, impurities were scrubbed by 4 M HNO$_3$ in two cycles. Results revealed that approximately 74% of Zr(IV) was separated to the organic phase and 26% remained in the aqueous phase. Determination of impurities after separation from the Zr matrix by ICP-MS using internal standard in revealed that the recovery of impurities achieved 95–100%. With the mentioned amount of Zr, the effect of the Zr matrix on the determination of elements by ICP-MS is negligible. Levels of impurities have relative standard deviations (RSD) of less than 6.9% and recovery of 88.6–98.8%. Therefore, the determination of impurities has high reliability and accuracy. The back-extraction of Zr(IV) in organic phase by 1 M H$_2$SO$_4$ has stripped about 99.5% of the Zr matrix back to the aqueous phase. Following this, NH$_3$ was added to the solution containing Zr after back-extraction to form Zr(OH)$_4$ which was then desiccated to produce ZrO$_2$. X-ray Diffraction (XRD), Scanning and Transmission Electron Microscopy (SEM and TEM) images showed that the new ZrO$_2$ product has spherical nanostructure with diameters of less than 25 nm, which is suitable for applications for the treatment of colorants, metal ions in wastewater sources and manufacture of anti-corrosion steel. In addition, the energy dispersive X-ray (EDX) of the new ZrO$_2$ product showed that it has high purity.

Keywords: impurities; high purity Zr; extraction; PC88A; ICP-MS; nano ZrO$_2$

1. Introduction

Recently, nuclear energy, despite its safety concerns, has been considered as a viable and practical source of energy. Zirconium materials with high purity, thanks to their excellent corrosion resistance and low neutron absorption cross-section (0.18 barn), have been used as the fuel elements, in reactor cans and pressure tubes for nuclear reactors. Although some Zr-based materials (e.g., metal, oxide, and alloys) have very high purity, those samples still contain many impurities with different levels [1–4]. The presence of such impurities could damage valuable properties of Zr. For example, one notable feature of the material, the transparency with thermal neutrons, when tarnished, could adversely affect the properties of the material and reduce the efficiency of the nuclear reactor. Therefore, specifications of the alloys must be strictly controlled and materials with high neutron absorption cross-section such as Hf, B, Cd, Gd, and Sm are required. To achieve this, it is necessary to analyze impurities in high-purity Zr materials before they are used in nuclear reactors [5–8].

Inductively coupled plasma mass spectrometry (ICP-MS) is a modern analytical method having the advantages of high sensitivity, low spectral interference, and low matrix effects. Some applications of ICP-MS for determination of impurities in Zr materials (ZrO_2, Zircaloy 360a, $ZrOCl_2$, $ZrCl_4$) are detailed in many studies [5–13]. Impurities (or trace elements) with high content can be directly determined by ICP-MS using matching matrix and internal standard (e.g., In, Bi, Rh). However, impurities of traces and super traces need to be separated from the matrix to prevent them from being interfered by matrix influence which in turn allows for impurity determination by ICP-MS using the internal standard. Regarding separation of the matrix, several authors proposed the separation of the Zr matrix by solvent extraction and determination of impurities after separation of the matrix by ICP-MS. Solvent extraction has been regarded as one of the most promising operations to the separation of the Zr matrix from metallic elements due to its great technical ease of being carried out in a continuous mode.

In our previous study [5], 15 trace rare earth impurities were determined in high-purity ZrO_2 by ICP-MS after separation by solvent extraction using 0.1 M PMBP/toluene. In addition, approximately 99.7% of Zr matrix was extracted from 2 M HNO_3 and impurities have been determined with RSD of less than 14% and Rev ranging from 89 to 110%. In the similar investigation with regard to zircaloys [7], many impurities have been determined by isotope dilution—ICP-MS after removal of the Zr matrix by liquid-liquid extraction using D2EHPA/toluene. In this research, the Zr matrix was extracted from HNO_3 with pH = 2 and 16 impurities that have been fully scrubbed by 6 M HNO_3. For high-purity zirconium oxide, trace impurities in three samples have been found by high-resolution-ICP-MS with the internal-standard (In) and standard addition methods [8]. Some impurities in zircalloy-2 samples have been also determined by ICP-MS with the internal-standard (Rh), standard addition and calibration methods [9].

Liquid-liquid extraction (or solvent extraction) is usually used to separate the Zr matrix from other elements by extractants such as Cyanex921, D2EHPA, TBP, 2-octylamino piridine, *N-n*-octylaniline, PC88A, Cyanex272, LIX 84-IC, TOPO (- TrisOctyl Phosphin Oxide), DIBK (- Di Iso Buthyl Keton) and BAEP (-bis(2-ethylhexyl)-1-(2-ethylhexylamino)propylphosphonate) [14–27]. A closer search of literature indicates that the use of di-2-ethylhexylphosphonic (PC88A) as an extractant for the solvent extraction of Zr(IV) from acid solutions was scarce [10,20,28]. PC88A is an acid extractant (pK_a = 4.1 in methanol) having molecular formula of $C_{16}H_{35}PO_3$ (M = 306.43 g/mol), with structural formula shown in Figure 1.
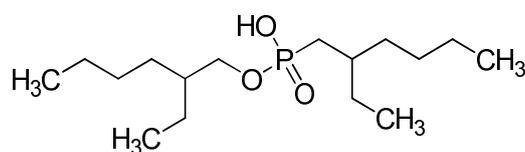

Figure 1. Structural formula of di-2-ethylhexylphosphonic (PC88A).

Previous studies have investigated the separation of the matrix zirconium from other impurities by solvent extraction using solvents including PC88A in kerosene and showed remarkable results for the determination of impurities in high-purity $ZrCl_4$ [10].

Nanoscale materials and ZrO_2 nanoparticles have been explored for the treatment of Cr (III), Cr (VI), and other ions in wastewater, achieving generally positive results [29,30]. In addition, fabricating ZrO_2 nanoparticles and ZrO_2 nanoparticles/silane on the surface of steel results in increased adhesion between the steel surface and the coating and approximately two-fold to three-fold improvement in corrosion resistance of the steel [31,32].

Although PC88A has been known as an extractant for trace amounts of Zr(IV), its application for removing Zr matrix from a dissolved ZrO_2 sample has not been thoroughly studied. To be specific, except for one particular study where Cyanex921 is used as the extractant [15], literature relating to this paper only concerns determination of impurities in ZrO_2 and Zircaloys by HR-ICP-MS or ICP-MS [7–9], or determination of impurities by ICP-MS after separation of the matrix by liquid-liquid extraction [5,6], or optimal conditions for extraction of Zr(IV) [16–25] and therefore lacks results on nano ZrO_2 purification. Therefore, the main objective of this work is two-fold. First, we attempt to determine impurities in high-purity ZrO_2 material by ICP-MS after separation of the Zr matrix from nitrate using solvent extraction with PC88A dissolved in toluene. Second, synthesis of ZrO_2 nanoparticles of high-purity was conducted. The results could act as a precursor for application of ZrO_2 nanoparticles in treatment of color compounds (e.g., crystal violet, methylene blue) [33,34], metal ions in wastewater and enhancement of adhesion between the steel surface and the coating.

2. Materials and Methods

2.1. Chemicals, Materials, and Instruments

PC88A (2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester, 98%, Daihachi, Osaka, Japan) and toluene (Merck, Darmstadt, Germany) were used as an extractant and diluent, respectively. $ZrCl_4$ (Merck, 98%) and ZrO_2 (Institute for Technology of Radioactive and Rare Elements—ITRRE) was used as a source of Zr(IV). Other reagents included Zr(IV), Hf(IV), Ti(IV), In(III) standard solutions (1000 µg/mL) and multi-element standard solution of 43 elements (including 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 and 14 rare earth elements) 1000 µg/mL; Super pure HNO_3, $HClO_4$ and ultra water 18 MΩ. All reagents are of analytical grade and were purchased from Merck, Germany.

The IR, UV spectra of salt, solvent, and complex were recorded using FT-IR (Spectrum Two, PerkinElmer, Akron, OH, USA) and UV-1700 (Shimadzu, Kyoto, Japan) spectrometer. The concentrations of zirconium and other elements in the aqueous phases were determined by ICP-MS (NexION 300Q, PerkinElmer, Akron, OH, USA) instrument. Other apparatuses such as funnels and shaker were also used in the study.

Characterization of the produced ZrO_2 was done using a number of techniques. Labsys TG/DSC-TGA-Setaram heat analyzer (Caluire, France) with a heating rate of 5 °C/min in air environment from 30 to 800 °C was used to obtain the thermal schematic of $Zr(OH)_4$. Energy Dispersive X-ray spectroscopy (EDX, module ISIS 300 Oxford England) was used to determine the level of elements. The X-ray Diffraction (XRD) patterns of the product were collected at room temperature using a D8 Advance (Germany) with λ = 0.154056 nm ($CuK_{\alpha 1-}$ radiation). The morphology was studied using scanning and transmission electron microscopy (SEM and 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, Redding, CA, USA) in ethanol-diluted samples for approximately 2 min. SEM images were obtained using a S4800-Hitachi (Hitachi High-Technologies Corporation, Kyoto, Japan) operating at 5 kV.

2.2. Analytic Methods for Separation of Zr(IV) and Determination of Impurities

Dissolution procedure: 0.0845 g of ZrO_2 powder (Institute for Technology of Radioactive and Rare Elements—ITRRE, Hanoi, Vietnam) was weighed and dissolved in 5 mL of concentrated HNO_3, 3 mL of concentrated HCl, 1 mL of concentrated HF and boiled at 180 °C in a steel bomb until the sample is completely dissolved. 2 mL of concentrated HNO_3 was added and the solution was boiled to remove excess HF acid. The solution was heated slowly, dissolved and added up to the mark 25 mL by 0.3 M and 3 M HNO_3. The concentration of Zr(IV) in these solutions was 25 mg/mL.

Separation of Zr(IV) from HNO_3 media by PC88A/toluene solvent: Aqueous phase contained 25 mg/mL Zr(IV) and other impurities in 3 M HNO_3 media. The organic phase was 50% PC88A in toluene. Equal volumes of the aqueous phase and organic phase were contacted for 60 min with a mechanical shaker, equilibrated for 30 min at room temperature (25 ± 0.5 °C) unless stated otherwise. The aqueous phase was separated and the organic phase was scrubbed of elements for 2 cycles by 4 M HNO_3 solutions. The aqueous phase and scrubbing solutions were subsequently mixed, added with 5 mL of (25% HNO_3 + 20% $HClO_4$) solutions, evaporated to dryness, then added by internal standard In and dissolved in 0.3 M HNO_3 solutions to the volume of 10 mL for measurements on ICP-MS (NexION 300Q, PerkinElmer, USA) for determination of impurities.

Characterization of ZrO_2 product after solvent extraction using PC88A/toluene: Fixed volume of the aqueous phase (1.0 M H_2SO_4) was contacted for 60 min with different volumes of the loaded PC88A until equilibrium is achieved. Lastly, a fixed phase ratio (A:O) of 1:1 was kept for 2 cycles to achieve the highest stripping efficiency of Zr back to the aqueous phase (Table 1). A measured portion of the aqueous phase was taken for zirconium analysis. After the stripping process, the aqueous solution of zirconium was adjusted by the ammonia solution to pH = 9 to precipitate $Zr(OH)_4$. The precipitate was filtrated and dried at 60 °C overnight, then desiccated at 500–800 °C for 3 h to form ZrO_2 which was used for complete characterization.

3. Results and Discussion

3.1. IR, UV Spectral Studies of $ZrO(NO_3)_2$ Salt, PC88A–Toluene Solvent, and the Extracted Complex Zr–PC88A

The study on extraction capability of Zr(IV) by PC88A was examined by infrared spectrum (IR) of $ZrO(NO_3)_2$, PC88A–toluene and Zr–HNO_3–PC88A-toluene. IR and UV spectra of the salt, solvent, and the extracted complex are showed in Figures 2 and 3.
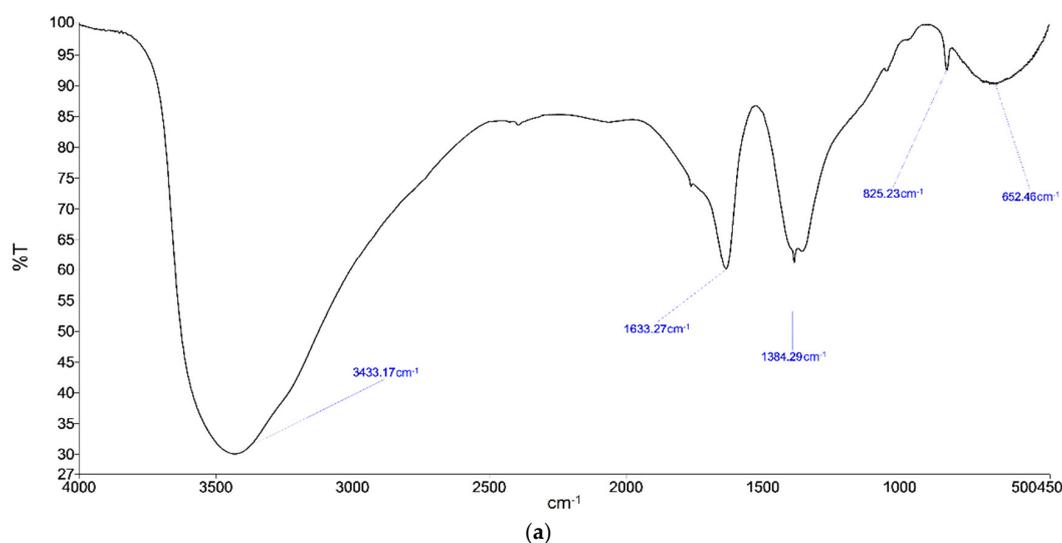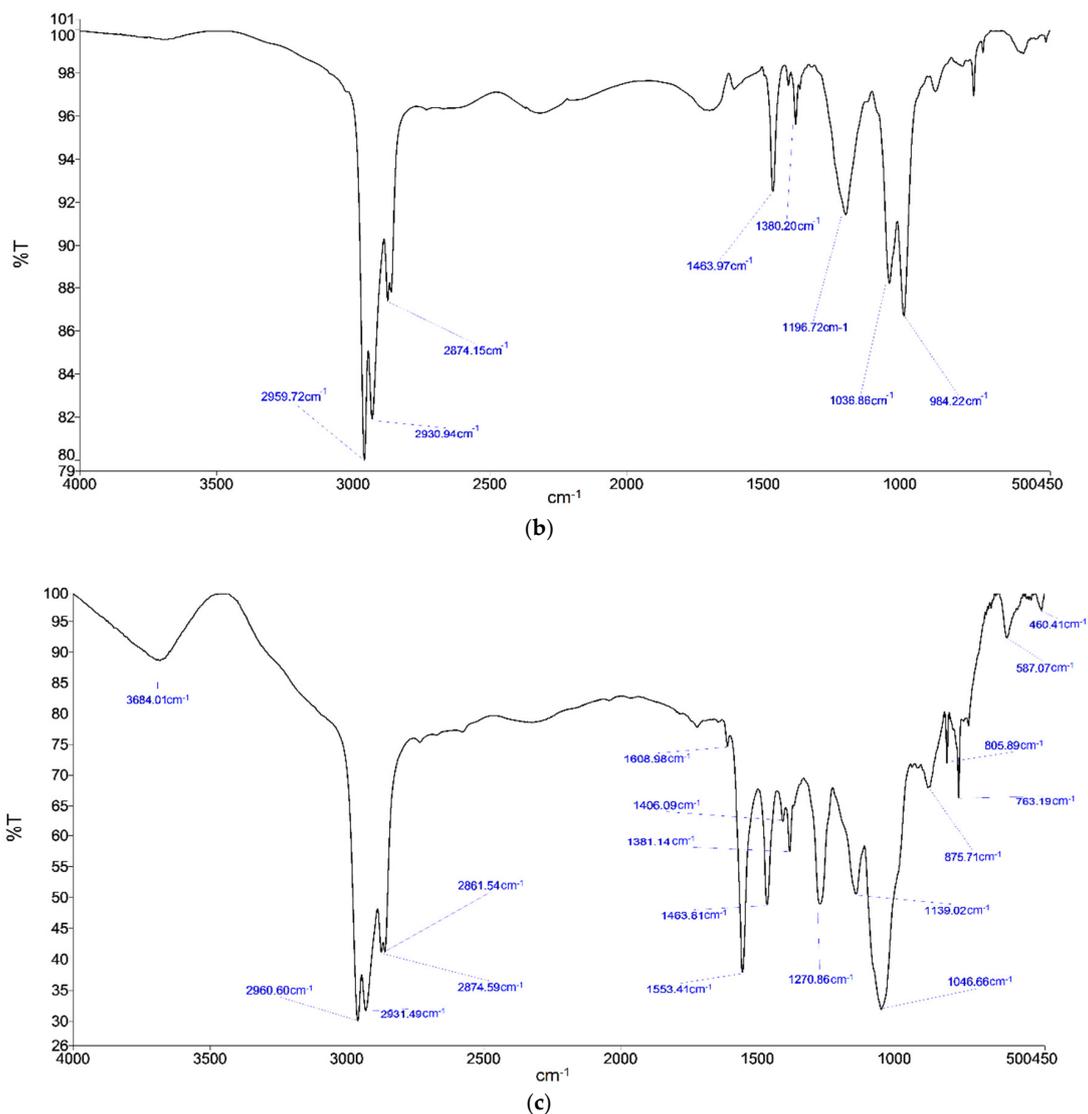

(a)

Figure 2. *Cont.*

(b)

(c)

Figure 2. FT-IR of (**a**) Zr(IV)-HNO$_3$; (**b**) PC88A-toluene and (**c**) Zr-PC88A complex.
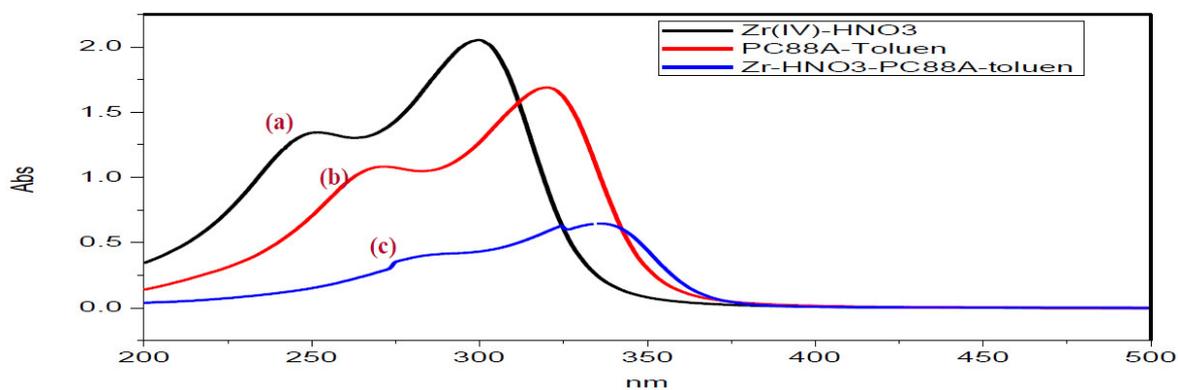

Figure 3. UV spectrum of: (a) Zr(IV)–HNO$_3$; (b) PC88A-toluene; and (c) Zr-PC88A.

The infrared spectra of Zr(IV)–HNO$_3$, PC88A–toluene and Zr-PC88A–toluene complex were recorded. The infrared band at 1633.27 cm^{-1} for NO$_3^-$ in ZrO(NO$_3$)$_2$ was transferred to 1608.98 cm^{-1} in the Zr–PC88A complex. In addition, the infrared band at 1196.72 cm^{-1} for P=O vibration in PC88A is split into two bands at 1139.02 and 1270.86 cm^{-1} in the complex. Besides, the infrared band at

1036.86 cm^{-1} for P–O–CH$_2$ vibration in PC88A is transferred bands at 1046.66 cm^{-1} in the complex. These strong translations indicate that both ions of the ion pair have probably created strong bonds. In other words, there was coordination of phosphoryl oxygen atom and Zr(IV) and NO$_3$$^-$. This result shows that there is a strong interaction between PC88A and Zr(IV) in HNO$_3$ media. This is consistent with a previous study, which studied complex of Zr(IV) in HCl, H$_2$SO$_4$ acid with PC88A, BEAP [20,27].

The UV spectrum of Zr(IV) has two maxima at 237.5 and 294.5 nm. The UV spectrum of PC88A–toluene has two maxima at 262.5 and 319 nm. The UV of Zr–PC88A, on the contrary, only has one maximum at 337.5 nm. These translations show that there was a strong interaction between (-P=O) of PC88A and Zr(IV) in HNO$_3$ media. This result was consistent with an IR spectral study [20]. The extraction of Zr(IV) from the aqueous solution with nitric acid concentration using PC88A can be expressed by the following equation:

$$ZrO^{2+} + 2NO_3{}^- + 2PC88A \rightarrow ZrO(NO_3)_2 \cdot 2PC88A \tag{1}$$

3.2. Stripping of Zirconium from Loaded PC88A/Toluene

After extraction of Zr(IV) in 3 M HNO$_3$ by 50% PC88A/toluene, we back-extracted Zr(IV) to the aqueous phase. All the experiments were performed on the stock organic solution PC88A. A mixture of 10 mL of the loaded organic (24.950 mg/mL) of Zr(IV) and certain volume of stripping agent (maintaining the required phase ratio) was vigorously shaken in 60 mL funnel and at room temperature for 60 min of contact time, followed by 30 min of equilibrium. The aqueous and organic phases were separated and the aqueous phases were analyzed by Zr(IV). Results of stripping of zirconium from loaded PC88A/toluene with 20 extraction solutions are showed in Table 1.

Table 1. Stripping efficiency (%) of Zr(IV) from loaded 50% PC88A/toluene with some extraction solutions.

No.	Extraction Solutions	Stripping Efficiency (%)	No.	Extraction Solutions	Stripping Efficiency (%)
1	1 M HCl	25.5	11	3 M HNO$_3$	4.7
2	2 M HCl	30.0	12	4 M HNO$_3$	6.4
3	3 M HCl	31.5	13	1 M HCl + 1% H$_2$O$_2$	31.0
4	4 M HCl	32.8	14	2 M HCl + 1% H$_2$O$_2$	42.5
5	0.1 M H$_2$SO$_4$	96.5	15	1 M HCl + 2% H$_2$O$_2$	41.0
6	0.3 M H$_2$SO$_4$	97.0	16	2 M HCl + 2% H$_2$O$_2$	52.0
7	0.5 M H$_2$SO$_4$	98.0	17	2 M HNO$_3$ + 1% H$_2$O$_2$	6.5
8	1.0 M H$_2$SO$_4$	99.5	18	4 M HNO$_3$ + 1% H$_2$O$_2$	17.5
9	1 M HNO$_3$	3.1	19	2 M HNO$_3$ + 2% H$_2$O$_2$	6.2
10	2 M HNO$_3$	4.4	20	4 M HNO$_3$ + 2% H$_2$O$_2$	18.0

As shown in Table 1, H$_2$SO$_4$ is the most effective stripping agent for stripping of zirconium from loaded PC88A/toluene. The feasibility of using PC88A for separation of zirconium was assisted by stripping studies. Thus, the scrubbing extraction using 4 M HNO$_3$ solutions to effectively remove the Zr(IV) matrix and determine impurities is the most suitable method. The loaded zirconium onto PC88A/toluene has been stripped with stripping efficiency of 99.5% when using 1.0 M H$_2$SO$_4$ as an efficient eluting agent at 60 min of contact time and phase ratio O:A (v/v) as 1:1.

The stripping efficiency largely depends on the stripping solution. Due to the stability of the Zr-PC88A complex in the organic phase, as demonstrated by IR and UV spectra, it is necessary to use stripping solution that is highly acidic or antioxidant or both to destabilize the complex. Therefore, H$_2$SO$_4$ with concentration of higher than 1 M could achieve the highest stripping efficiency after two cycles [20]. The initial concentration of zirconium in aqueous phase (before solvent extraction) was 25.000 mg/mL. Determined concentrations of Zr in organic phase after extraction and in aqueous phase after two cycles of stripping with 1 M H$_2$SO$_4$ were 24.950 mg/mL and 24.826 mg/mL, respectively. The

stripping extraction of Zr(IV) from the organic phase using H_2SO_4 can be expressed by the following equation:

$$ZrO(NO_3)_2 \cdot 2PC88A + 2H_2SO_4 \rightarrow H_2ZrO(SO_4)_2 + 2HNO_3 + 2PC88A \tag{2}$$

3.3. Separation of Impurities from the Zr(IV) Matrix by Solvent Extraction with 50% PC88A/Toluene

ICP-MS using matching matrix and internal standard could directly determine some impurities of high content in high-purity ZrO_2. However, trace impurities need to be separated from the Zr matrix to eliminate the interference of the matrix and determine them by ICP-MS using the internal standard (as In, Bi, Rh). Extraction and scrubbing extraction can be used for separation of impurities from the Zr(IV) matrix in materials of nuclear grade and high-purity zirconium.

From stripping results of Zr(IV), we chose 4 M HNO_3 solutions for two stripping cycles of impurities after extraction process containing 25 mg/mL Zr(IV) and 0.5 μg/L of each impurity from 3 M HNO_3. The analytic results of elements by ICP-MS in the aqueous phase and organic phase are shown in Table 2.

Table 2. Contents of elements in the aqueous phase and organic phase after 1 extraction by 3 M HNO_3 and 2 scrubbing cycles by 4 M HNO_3 using 50% PC88A/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	95.5	97.6	71.7	34.2	26
Organic phase, %	Not detected	4.5	2.4	28.3	65.8	74

As shown in Table 2, after 1 cycle of extraction by 3 M HNO_3 and two cycles of scrubbing by 4 M HNO_3 solutions, the recoveries were found at 95–100%. 41 elements were separated and Zr remaining in the aqueous phase was about 26%. It was found that with the mentioned amount of Zr, the effect of Zr on the determination of elements except Hf, Ti, and Fe by ICP-MS is negligible. Therefore, this extraction system can be used for determination of impurities in materials of nuclear grade and high-purity zirconium by ICP-MS.

3.4. Determination of Many Impurities in High-Purity ZrO_2 by ICP-MS after Separation of the Matrix

We first applied the process of separation of Zr matrix and determination of impurities into the certified reference sample (SRM-zircaloy 360b). The results were in good agreement with the certified values [2].

The aforementioned process was then applied to analyze the ZrO_2 sample (ITRRE). Solvent of 50% PC88A/toluene was used to remove the Zr matrix from 3 M HNO_3 solutions, then 4 M HNO_3 solutions were used for scrubbing extraction of the organic phase in two cycles. Table 3 shows the results of determination of many impurities (Ims) by ICP-MS after separation of the matrix (with the standard additional method and an internal standard of 150 μg/L In) in high-purity ZrO_2 ITRRE (repeated three times). The (a) value of impurities was determined after extraction of Zr(IV) by extractants such as TBP, D2EHPA, PC88A (repeated three times for each extractant).

As shown in Table 3, the levels of impurities in ZrO_2 with three replicates ($n = 3$) vary from 0.0003 μg/g for Tl to 5.3927 μg/g for Ag, in which their total amount is lower than 1.8%. Thus, from the standard of nuclear grade, the ZrO_2 material had high purity (98.2%). From the results of the determination of impurities after separation of the Zr matrix using 50% PC88A/toluene by ICP-MS, the recovery is shown to vary from 88.6 to 98.8% for different impurities. The %RSD of the impurities varies from 0.2 to 6.9%. The Student's *t*-test shows that t_T value was less than $t_{(0.95; 2)} = 4.3$, thus the determination results after separation of the zirconium matrix are highly accurate and well-matched to the certified values of high-purity zirconium materials [1–4].

Table 3. Levels of impurities in high-purity ZrO$_2$ (ITRRE) after separation of the Zr (IV) matrix by 50% PC88A/toluene.

No.	Ims	Mass	Levels ($\overline{X}$) (µg/g)	RSD, %	$S_{\overline{X}}$	Known Value (a)	$t_T = \frac{\overline{X}-a}{S_{\overline{X}}}$	Added (µg/g)	Total (µg/g)	Rev (%)
1	As	75	0.021 ± 0.002	1.2	0.021	0.021	0.007	1.0	1.040	96.4
2	Cd	111	1.085 ± 0.065	0.8	0.014	1.081	−0.001	2.5	4.592	95.4
3	Pb	208	0.020 ± 0.000	0.2	0.004	0.020	−0.045	1.0	1.038	95.5
4	Cu	63	0.006 ± 0.001	1.5	0.026	0.006	0.002	1.0	1.011	94.7
5	Cr	53	0.030 ± 0.003	1.5	0.026	0.031	−0.017	1.0	1.059	94.7
6	Ni	60	0.005 ± 0.000	0.6	0.010	0.005	0.003	1.0	1.009	94.7
7	Hg	202	-	6.9	0.172	-	-	1.0	1.001	88.6
8	Mn	55	0.022 ± 0.002	1.1	0.019	0.022	−0.002	1.0	1.041	96.3
9	Zn	66	0.071 ± 0.007	1.3	0.023	0.071	0.025	1.0	1.136	95.3
10	Co	59	0.000 ± 0.000	0.9	0.016	0.000	−0.001	1.0	1.001	94.0
11	Fe	57	0.386 ± 0.052	1.8	0.031	0.404	−0.555	1.0	1.812	98.5
12	Be	9	0.001 ± 0.002	6.2	0.107	0.001	−0.000	1.0	1.001	94.4
13	Li	7	0.000 ± 0.000	1.2	0.021	0.000	0.000	1.0	1.001	94.0
14	Mo	100	0.001 ± 0.000	5.0	0.081	0.001	−0.002	1.0	1.001	93.8
15	Ag	107	5.393 ± 0.442	1.1	0.019	5.412	−0.995	5.0	21.119	98.8
16	Sb	121	0.002 ± 0.000	0.4	0.007	0.002	0.002	1.0	1.003	93.3
17	Se	82	0.002 ± 0.001	7.9	0.137	0.002	0.000	1.0	1.004	92.9
18	Sr	88	0.016 ± 0.001	0.5	0.009	0.016	0.021	1.0	1.031	95.0
19	Ti	49	1.290 ± 0.307	3.2	0.055	1.292	−0.045	2.5	5.180	99.0
20	Tl	205	0.000 ± 0.000	4.8	0.083	0.000	−0.001	1.0	1.001	90.0
21	V	51	0.028 ± 0.002	1.1	0.019	0.028	−0.009	1.0	1.056	96.1
22	Ba	137	0.056 ± 0.001	0.3	0.005	0.056	0.101	1.0	1.108	95.8
23	Mg	24	0.192 ± 0.010	0.7	0.012	0.194	−0.207	1.0	1.372	97.2
24	Ca	43	3.221 ± 0.336	1.4	0.024	3.275	−2.240	5.0	11.549	98.1
25	Sn	118	0.004 ± 0.000	1.1	0.019	0.004	−0.007	1.0	1.008	95.0
26	REEs		5.766 ± 1.031	2.4	0.042	5.802	−0.863	5.0	10.281	95.5

In comparison with previous works, some main points are drawn as follows in Table 4.

Table 4. Comparison of results of related studies.

	Previous Works				This Study
	[5]	[7]	[8]	[9]	
Similarity	The impurity determination procedure applied in this study is similar to that of previous works [5,7–9] where Zr matrix is separated before determination by ICP-MS				
Extraction Agent	1-phenyl-3-methyl-4-benzoyl-5-pyrazone (PMBP)	Bis-2-(ethylhexyl) ortho phosphoric acid (D2EPHA)	Direct determination by HR-ICP-MS	Direct determination some elements of high content	2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC88A)
Diluent	toluene	toluene			toluene
Extraction Solutions	2 M HNO_3	HNO_3 pH = 2			3 M HNO_3
Scrubbing Solutions		6 M HNO_3			4 M HNO_3
Stripping Solutions					1 M H_2SO_4
Impurities, Rev (%)	15 REEs impurities (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu); RSD < 14%; Rev = 89–110%; LOD = 1.8–5.7 µg/g	16 impurities (Ni, Cu, Zn, Ag, Cd, Pb, Tl, U, Ce, Dy, Er, Eu, Gd, Nd, Sm, Yb)	17 impurities (Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Sr, Cs, La, Ce, Hf, Pb, Bi); LOD = 0.01–9 µg/g	5 impurities (Ti, Cr, Mn, Fe, Cu); RSD < 5%	40 impurities (see Table 3); RSD ≤ 6.9%; Rev = 88.57–98.8%
Material/Method	High-purity ZrO_2/ICP-MS	Zircaloys/isotope dilution-ICP-MS	Three high-purity ZrO_2 samples/HR-ICP-MS with the internal—standard (In), standard addition methods	Zircalloy-2/ICP-MS with the internal-standard (Rh), standard addition and calibration methods	ZrO_2 (from Institute for Technology of Radioactive and Rare Elements-ITRRE, Vietnam)/ICP-MS with the internal—standard (In), standard addition and calibration methods

The proposed procedure is advantageous 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 (National Institute of Standards & Technology, Gaithersburg, MA, USA) namely ZrO_2, $ZrO(NO_3)_2$, $ZrOCl_2$, Zircaloy-2, Zircaloy-4 and Zircaloy 360a.

3.5. Characterization of ZrO_2 Product after Solvent Extraction by PC88A/Toluene

The TG/DSC-TGA, XRD, SEM, TEM, and EDX of the obtained ZrO_2 product after solvent extraction (SE) are showed on Figures 4–8.

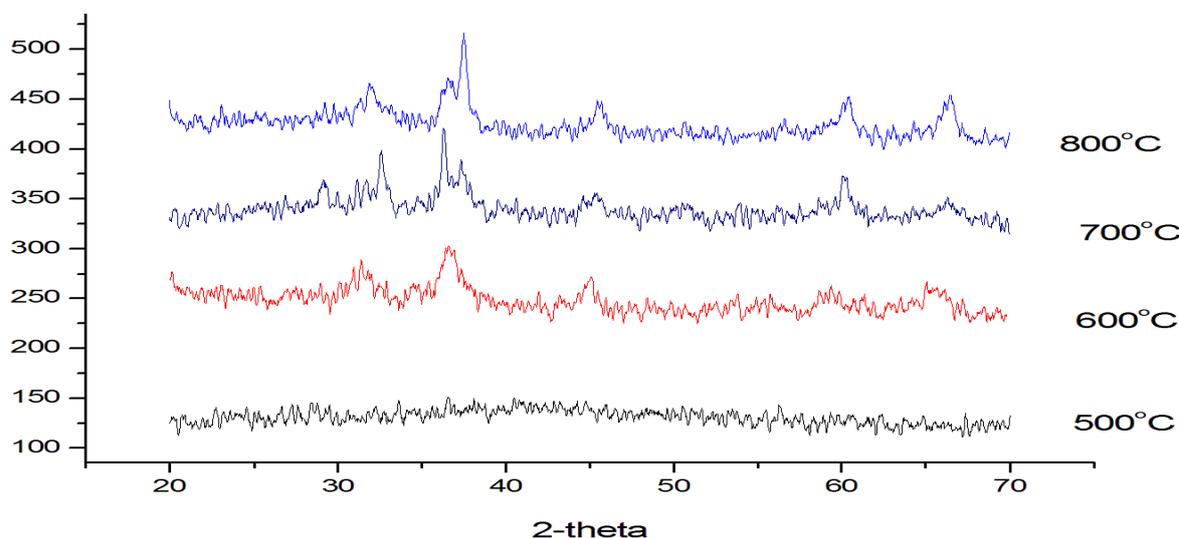**Figure 4.** Schematic of thermal analysis of $Zr(OH)_4$.

Figure 5. X-ray Diffraction (XRD) pattern of ZrO_2 product after SE by PC88A/toluene at 500–800 °C.
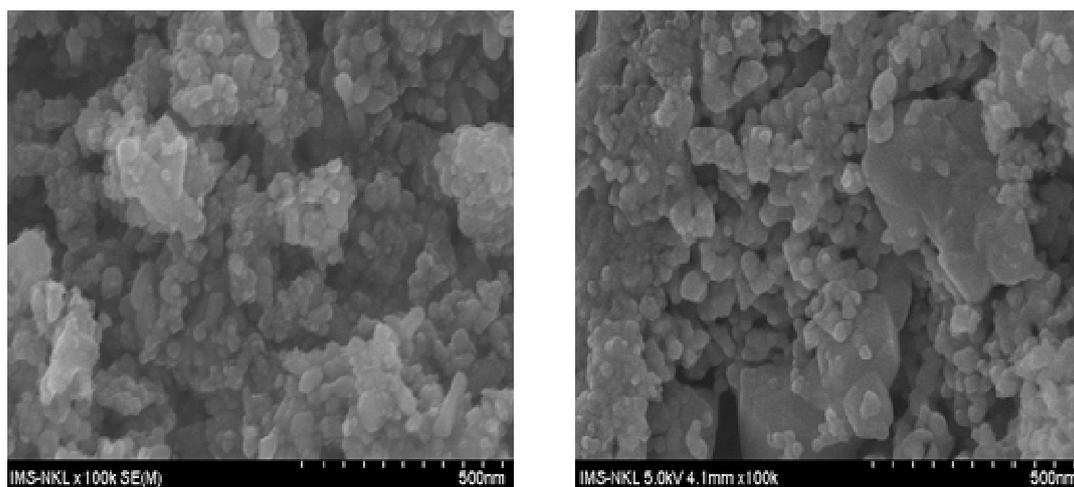
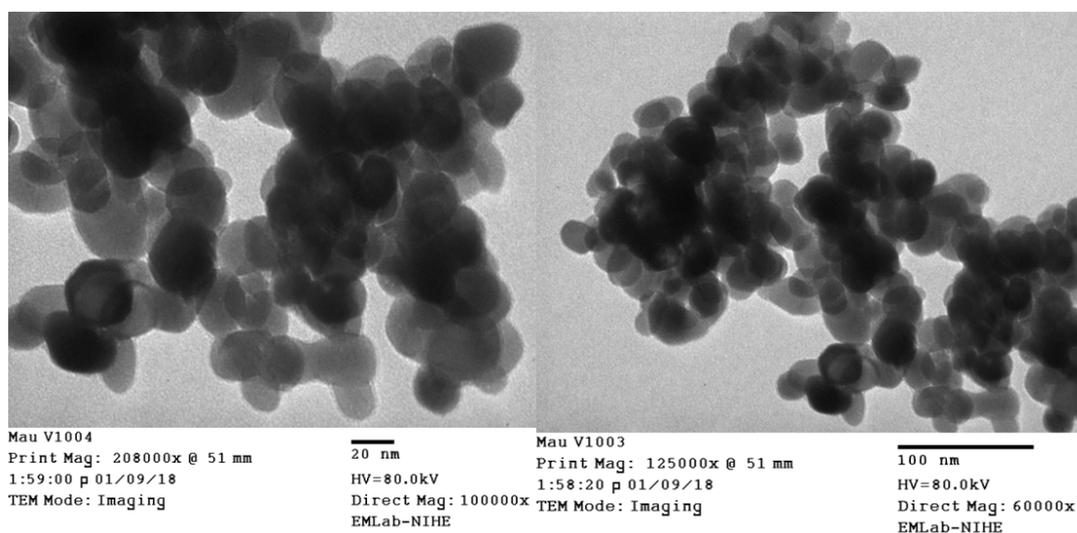**Figure 6.** SEM images of ZrO$_2$ product after SE by PC88A/toluene.

Figure 7. TEM images of ZrO$_2$ product after SE by PC88A/toluene.

Figure 8 indicates 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 PC88A/toluene has very high purity. This is consistent with the determination of the levels of impurities (in Table 3) of Section 3.4.
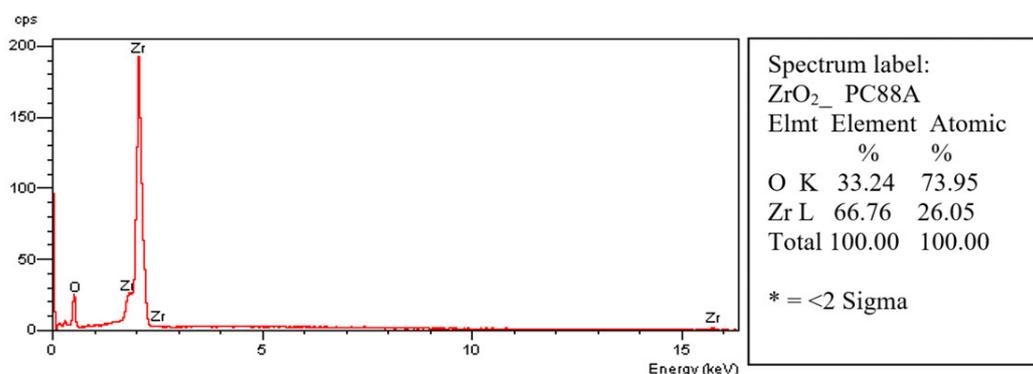

Figure 8. Energy dispersive X-ray (EDX) of ZrO$_2$ product after SE by PC88A/toluene.

As shown in Figure 4, the schematic thermal analysis of $Zr(OH)_4$ shows that when temperatures were higher than 300 °C, the mass of the sample is virtually unchanged. Therefore, we proceeded to heat samples at higher temperatures between 500–800 °C to obtain pure ZrO_2.

From the results shown in Figure 5, at 500 °C, the sample was still in an amorphous state. When increasing temperature to 600 °C, single-phase samples of ZrO_2 were obtained. The X-ray diffraction for zirconia sample at 600 °C indicates the presence of diagonal phase (t) of zirconium oxide as the major component with characteristic peak of the $d = 2.470$ facets at $2\theta = 36°$, which is obtained using Debye Scherer formula:

$$\bar{r} = \frac{0.9\lambda}{\beta \cos \theta} \tag{3}$$

where $\lambda = 1.54056$ nm is the X-ray wavelength, β is the Full-Width at Half-Maximum (FWHM) of the diffraction peak, and θ is the diffraction angle. The particle size of the formed zirconia from solvent extraction using PC88A/toluene was around 21.32 nm. Therefore, we can conclude that PC88A in these experiments acted as an extractor for zirconium and surfactant for the preparation of zirconium nanoparticles.

SEM and TEM images taken on zirconia sample in Figures 6 and 7 indicate that obtained particles have spherical form, are fairly uniformly distributed and have an average particle size of ≤ 25 nm. This is because PC88A in this experiment acts as extractor for zirconium and surfactant for the preparation of zirconium nanoparticles. Particle size determined by TEM images are quite consistent with the XRD spectra. The results of the use of ZrO_2 nanoparticles as materials for adsorption of colorants, treating metal ions in wastewater or fabricating the coatings prior to coating will be reported in subsequent studies.

In comparison with a previous study [15], we summarized some main points regarding the synthesis method and characterization of the nano ZrO_2 product as follows in Table 5.

Table 5. Comparison of synthesis methods and nano ZrO_2 product characterization of related studies.

	[15]	This Study
Extraction agent	Cyanex 921	2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester (PC88A)
Diluent	kerosene/decanol	toluene
Extraction solutions	HNO_3	3 M HNO_3
Scrubbing solutions		4 M HNO_3
Stripping solutions, efficiency (%)	1 M H_2SO_4—41.7%; 4 M H_2SO_4—72.1%	1 M H_2SO_4—99.5%
Material	Egyptian Rosetta zircon	ZrO_2 (ITRRE)
ZrO_2 purification	15–20 nm	21.32 nm
Optimum temperature	550 °C	600 °C
Purity of ZrO_2/method	105 ppm HfO_2, 99 ppm SiO_2, 76 ppm Al_2O_3, 48 ppm TiO_2, 880 ppm Fe_2O_3, 23 ppm MgO, 23 ppm CaO and 87 ppm P_2O_5/ICP (Inductively Coupled Plasma)	$\approx 100\%$ ZrO_2 (including 66.76% Zr + 33.24% O)

4. Conclusions

The strong extraction capability of Zr (IV) by PC88A was revealed by checking the IR and UV spectra of $ZrO(NO_3)_2$, PC88A-toluene and Zr-PC88A. Impurities after separation of the matrix Zr by 50% PC88A/toluene (using standard addition and internal standard In) in high-purity ZrO_2 powders were determined by ICP-MS. The values of RSD were less than 6.9% and Rev of 88.6 to 98.8%. All the

t_T test values were lower than the t-distribution critical value corresponding to 95% confidence level and 2 degrees of freedom ($t_{(0.95;\ 2)}$ = 4.3).

By using extraction and scrubbing extraction, stripping efficiency of the Zr matrix back to the aqueous phase was very high, at 99.5%, and a new ZrO_2 product was obtained. The XRD, SEM, and TEM analyses show that the new ZrO_2 product has spherical nanostructure, which is applicable to the adsorption of colorants or treatment of metal ions in wastewater sources and anti-corrosion steel. The EDX also showed that ZrO_2 product had a very high purity of nearly 100%.

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