Journal Homepage: - www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
Article DOI: 10.21474/IJAR01/6100
DOI URL: http://dx.doi.org/10.21474/IJAR01/6100

RESEARCH ARTICLE

INVESTIGATION OF DIRECT DETEMINATION OF MANY IMPURITIES IN HIGH PURITY $ZrCl_4$ MATERIAL AND AFTER SEPARATION OF THE MATRIX Zr USING SOLVENT EXTRACTION USING 2-ETHYL HEXYL PHOSPHONIC ACID MONO 2-ETHYL HEXYL ESTER (PC88A) BY ICP-MS.

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Manuscript Info

Manuscript History

Received: 19 October 2017
Final Accepted: 20 November 2017
Published: December 2017

Keywords:-
Impurities, $ZrCl_4$ material, extraction, PC88A, HNO_3, ICP-MS.

Abstract

ICP-MS using matching matrix and internal standard In is believed direct detemination some impurities such as Al, Si, Ti, V, Cr, Fe, Ni, Zn, Nb, Mo, Sn, Hf, Ta and W in high purity $ZrCl_4$. The study on capability extraction of Zr(IV) by di-2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester (PC88A) were examined by infrared spectrum (IR) of $ZrO(NO_3)_2$, PC88A-kerosene and Zr-PC88A-kerosene. Impurities in $ZrCl_4$ were also determinated when using internal standard In after separation of them from the matrix Zr by extracting in 50% of dissolved (PC88A) in kerosene. Investigation of separation of so many impurities from the matrix Zr showed that with using 50% PC88A/kerosene solvent, after one cycle extraction using 3M HNO_3 and 1-2 cycles stripping Zr and scrubbing impurities by 4M HNO_3 can recovery for 95-100% of almost investigated impurity elements and stripping about 22-28% of Zr(IV). 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 8.3% and recoveries (Rev) of 95.0-104.5%, so detemination of impurities was high reliability and accuracy.

Introduction:-

Zirconium (Zr) is a corrosion-resistant material with a low neutron absorption cross section (0.18 barn). It is not surprising that zirconium alloys have been widely used in nuclear industry, such as fuel elements, reactor cans and pressure tubes. Cited literature is need of all these alloys, Zircaloy-2 and Zircaloy-4 are particularly outstanding. The chemical composition and the trace elements that present in alloys substantially 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. According to the American Society for Testing and Materials (ASTM) standard methods (ASTM International, 2005), most trace elements such as Mn, Si, Cu, Ni, Cr, Ti and Fe in zirconium base alloy are determined individually by ultra-violet spectrometry after separation and some preconcentration through solvent extraction.

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Inductively coupled plasma mass spectrometry (ICP-MS) has the advantages of high sensitivity, low spectral interference and low matrix effects (Shen et al. 1990, Nakane 2004, Chen 2006). It is, therefore, attractive for the determination of these trace elements in zirconium base alloys, oxide and materials. A rapid determination can be achieved by simple dissolution of the samples and dilution of the solutions. Elements which are very difficult to separate chemically, such as Hf, or hardly present such as Mn, V, Sn, can be determined directly and accurately (Shen et al. 1990).

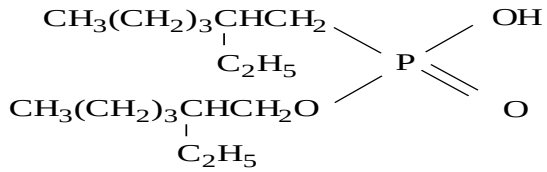
However, for ICP-MS due to the influence of the matrix, the determination of impurities in the Zr(IV) matrix will be deviate. Therefore, it is necessary to separate other impurities from the Zr(IV) matrix before determination of them by ICP-MS. For extraction of zirconium, numerous methods have been employed include: fractionated crystallization, precipitation, reduction, sublimation or distillation, absorption chromatography and ion exchangers. The distribution of solute between two immiscible solvents (liquid-liquid extraction) has been regarded as one of the most promising operation to separate the metallic elements due to its great technical ease of carrying out the continuous mode (A.S. El Shafie et all, 2014).

Nakane (2004) used high-resolution inductively to couple plasma mass spectrometry (HR-ICP-MS) for determination of trace impurities in high-purity ZrO_2. Most of the spectral interferences were avoided to use HR-ICP-MS. The method of internal standard In direct deteminated impurities such as Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Sr, Cs, La, Ce, Pb, Bi in three kinds of high purity ZrO_2 with LODs of 0.01 - 9 μg/g.

Shen et al. (1990) used ICP-MS to determine trace elements in NBS SRM 360a Zircaloy-2 (Zr-2) reference material. Accurate determination of Ti, Cr, Mn, Fe and Cu was achieved by using standard calibrations. The standard addition method was used to determine Hf. Standard addition results were also compared to Ti and Fe, which were not measured with the most abundant isotopes in direct calibration measurements. In both cases, the matrix Zr was not separated. The relative standard deviation was within 5%. Effects of an internal standard for ICP-MS with Zr matrix were also discussed.

Chen et al. (2006) was used ICP-MS for determination of trace rare earth elements (REEs) in high purity ZrO_2 after separation of the matrix by solvent extraction with 1-phenyl-3-methyl-4-benzoyl-5-pyrazone (PMBP) was used as extractant. In 2M HNO_3 solutions, it was found that more than 99.7% of the Zr matrix was removed. The main factors affected the extraction and determination, including acidity, the amount of PMBP and matrix concentration were investigated in details. In the optimal conditions, the determination limits were 1.8 - 5.7 μg/g in solid ZrO_2 with the relative standard deviations less than 14% and recovery of 89.0% - 110% for 14 rare Earth impurities.

Organophosphorus compounds includes TBP, D2EHPA and PC88A were effective extractants for tetravalent metals, particularly for zirconium (IV) by solvent extraction (Pandey et al. 1995, Biswas et al. 2002, B. Ramachandra Reddy et al. 2004, Blazheva et al. 2008, Le et al. 2014a, Le et al. 2014b, Chu 2015, Chu et al. 2017). A close 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 were scarce (B. Ramachandra Reddy et al. 2004, Le et al. 2014a, Chu 2015). PC88A is a new acid extractant (pK_a = 4.1 in methanol), molecular formula is $C_{16}H_{35}PO_3$ (M = 306.43 g/mol), with structural formula as follows:



In previous articles, the authors et all (Biswas et al. 2002, B. Ramachandra Reddy et al. 2004, Blazheva et al. 2008, Le et al. 2014a, Le et al. 2014b, Chu 2015) focused on separating of the matrix zirconium from other impurities by solvent extraction using solvents as tri-butyl phosphate (TBP) in toluene, di-2-ethylhexyl phosphoric acid (D2EHPA) in toluene and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (PC88A) in kerosene.

Recently, several authors combined the separation of the matrix Zr by solvent extraction and the 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 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. Although PC88A has been known long time ago as an extractant for trace amounts of Zr (B. Ramachandra Reddy et al. 2004), its application for removing Zr matrix from a dissolved $ZrCl_4$ sample was not studied. So, investigation of direct determination of many impurities in high purity $ZrCl_4$ material and after separation of the matrix Zr using solvent extraction with PC88A by ICP-MS has been done.

For these reasons, this investigation discusses the direct determination of impurities and determination after separation of the matrix zirconium from other elements in HNO_3 solutions with PC88A dissolved in kerosene by ICP-MS.

Materials and methods:-

Chemicals, materials and instruments:-

PC88A (di-2-ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester, 98%, Daihachi Chemical Industry, Japan) and kerosene 190-250^{0}C (Merck, Germany) were used as an extractant and diluents, respectively. 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; Super pure HNO_3, $HClO_4$ and ultra water 18 MΩ.

The IR spectrum of salt, solvent and complex were 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.

Analytic methods for Zr(IV) determination:-

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.

Separation of Zr(IV) from HNO_3 media by PC88A/toluene solvent:-

Aqueous phase containing 25 mg/mL Zr(IV) and other impurities in 3M HNO_3 media. Organic phase was 50% PC88A in kerosene. 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 4M HNO_3 solutions. Merged aqueous phase and stripping solutions, added 5 mL of (25% HNO_3+ 20% $HClO_4$) solutions, evaporated to dryness and dissolved in 0.3M HNO_3 solutions to volume of 10 mL for measuring on ICP-MS (Agilent 7500a) to determine of impurities.

Results and discussion:-

Direct determination of some impurities in high purity $ZrCl_4$ by ICP-MS:-

A inductively coupled plasma mass spectrometer (ICP-MS Agilent 7500a, USA) with a quadrupole mass analyzer 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
Carrier gas flow rate	1.2 L/ min
Auxiliary gas flow rate	0.9 L/min
Peripump rate	0.4rps
Time pump (uptake)	90s
Pump speed stability	0.1rps
Stable injection time (Stable)	30s
Coolant	2.4 L/min
Temperature spray chamber (S/C) and coolant	20^0 and 17^{0}C
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 (quadrupole analyzer)	7.3×10^{-3} Pa
Scanning (peak hopping)	
The pulse level	1000 V
The ion of lens	5.75 V
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

Direct determination results of some impurities in high purity $ZrCl_4$ with matching matrix and internal standard of 1000 µg/L In (repeat 3 times) by ICP-MS are presented in table 2.

Table 2:- Direct determination levels, relative standard deviation (RSD) and recovery (Rev) of impurities in high purity $ZrCl_4$

Impurities	Levels (µg/g)	RSD, %	Added (µg/g)	Total (µg/g)	Rev, %
Al	26.929±0.841	3.1	5.0	31.779	97.0
Ti	46.896±0.469	1.0	5.0	50.020	96.0
Si	278.974±23.12	8.29	25.0	291.699	95.6
V	16.525±0.460	2.8	5.0	21.275	95.0
Cr	23.072±0.815	3.5	5.0	28.172	102.0
Fe	31.387±0.410	1.31	5.0	35.123	96.0
Ni	38.211±0.895	2.3	5.0	43.436	104.5
Zn	50.714±1.675	3.3	5.0	55.484	95.4
Nb	26.674±0.845	3.2	5.0	31.484	96.2
Pb	36.778±0.241	0.66	5.0	40.380	96.2
Mo	16.567±0.423	2.6	5.0	21.367	96.0
Sn	12.674±0.484	3.8	5.0	17.454	95.6
Ta	36.816±0.318	0.86	5.0	40.196	95.6
W	26.991±0.272	1.0	5.0	30.857	95.8

The matrix effects of Zr were investigated and most of the spectral interferences were avoided by using internal standard element. In 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 Al, Si, Ti, V, Cr, Fe, Ni, Zn, Nb, Mo, Sn, Ta and W in high purity $ZrCl_4$ powders were presented in table 2. The values RSD <8.3% and Rev from 95.4 to 104.5%. 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 [12,13,14,15].

3.2. IR spectral studies of $ZrO(NO_3)_2$ salt, PC88A-kerosene solvent and the extracted complex Zr-PC88A-kerosene

The study on capability extraction of Zr(IV) by PC88A were examined by infrared spectrum (IR) of $ZrO(NO_3)_2$, PC88A-kerosene and Zr-HNO_3-PC88A-kerosene. IR of the salt, solvent and the extracted complex showed on figure

(a) (b)

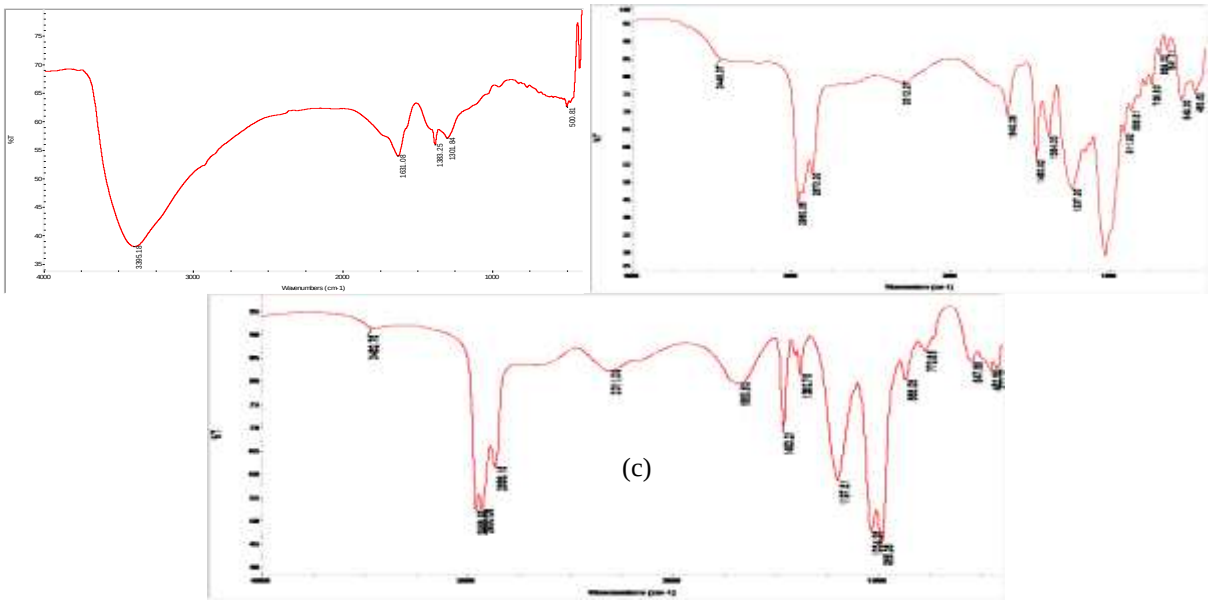
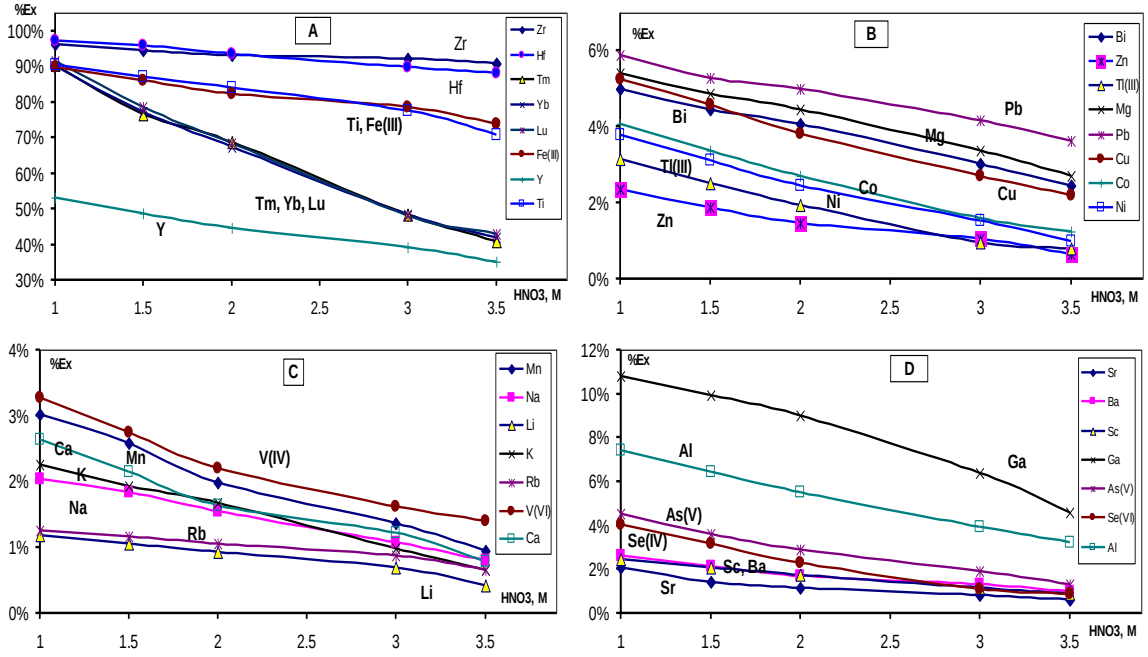


Fig.1:- Infrared spectrum of Zr(IV) (a), PC88A-kerosene (b) and Zr-HNO_3-PC88A-kerosene (c)

The infrared spectra of $ZrO(NO_3)_2$, PC88A-kerosene and Zr-PC88A complex were recorded. The infrared band at 1631.08 cm^{-1} for NO_3^- in $ZrO(NO_3)_2$ is transfer bands at 1483.21 cm^{-1} in the complex. Moreover, the infrared band at 1060 cm^{-1} for P=O vibration in PC88A-kerosene is split into two bands at 1034.28 and 980.08 cm^{-1} in the complex indicating that both ions of the ion pair are probably solvated. This result shows that there is strong complexity between PC88A and Zr(IV) in HNO_3 media. This result is consistent with the previous study [8].

The effects of HNO_3 concentration on extraction procedure by using 50% PC88A/kerosene solvent:-
Effects of (1-3.5M) HNO_3 on the extraction efficiency of Zr(IV) and other elements show on figure 2.



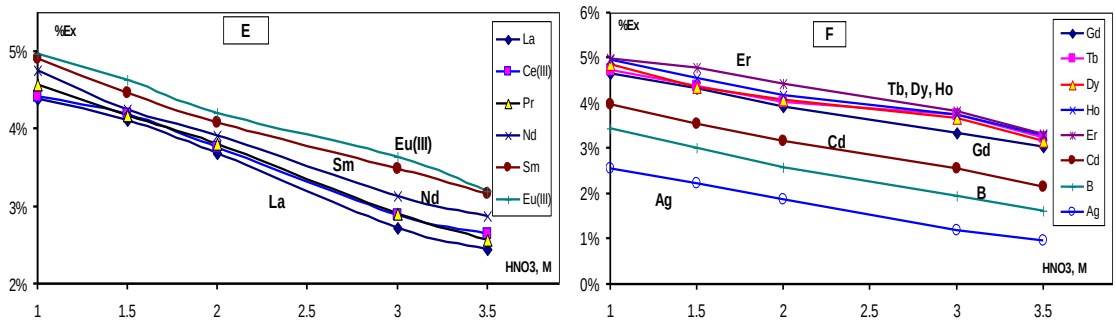


Fig.2:- Effects of (1-3.5M) HNO_3 concentrations on the extraction efficiency of Zr(IV) and other elements with 50% PC88A/kerosene solvent

A-the extraction efficiency of Zr, Hf, Tm, Yb, Lu, Fe,Y of Ti; B-the extraction efficiency of Bi, Zn, Tl, Mg, Pb, Cu, Co and Ni

C-the extraction efficiency of Mn, Na, Li, K, Rb, V and Ca; D-the extraction efficiency of Sr, Ba, Sc, Ga, As, Se and Al

E-the extraction efficiency of La, Ce,Pr, Nd,Pm, Sm and Eu; F-the extraction efficiency of Gd, Tb, Dy, Ho, Er, Cd, B and Ag

Figure 2 shows that when increasing HNO_3 concentration, the extraction efficiencies of Zr(IV), Hf(IV) were very high 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 96%, 98%, respectively, Y, Tm, Yb and Lu of 50-54%, Ti and Fe of 77.5 to 78.5%, Ga of 6.39% and extraction efficiencies of other elements were less than 4.17% with 3M HNO_3. The extraction efficiency of almost REEs was low (from 2.72 to 2.83%).

From stripping results of Zr(IV), we chose 4M HNO_3 solutions for 1 to 2 cycles stripping of impurities after extraction process containing of 25 mg/mL Zr and 0.5 µg/L 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 3 and table 4.

Table 3:- Contents of elements in aqueous phase and organic phase after 1 extraction by 3M HNO_3 and 1 stripping by 4M HNO_3 using 50% PC88A/kerosene

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	89	94	62	28	22
Organic phase,%	Not detected	11	06	38	72	78

Table 4:- Contented of elements in aqueous phase and organic phase after 1 extraction by 3M HNO_3 and 2 cycles stripping by 4M HNO_3 using 50% PC88A/kerosene

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	98	70	35	28
Organic phase, %	Not detected	05	02	30	65	72

Tables 3 and 4 were detected after 1 extraction by 3M and 1 to 2 cycles stripping by 4M HNO_3 solutions, the recoveries were found as 95-100% so that 41 elements could separated and Zr remained in water phase about 22-28%. 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.

Determination of other impurities in high purity $ZrCl_4$ by ICP-MS after separation of the matrix:-
Several methods can be used for the correction of matrix effects. Matching matrix is hampered, especially for the lower concentration levels as Zr sample of sufficient purity for this aim is not available. Standard additions are prone to errors as a result of spectral interferences. They can only be eliminated by separating the analysts from the Zr matrix, e.g. by solvent extraction or other methods.

Solvent of 50% PC88A/kerosene was used to removal of the matrix Zr from 3M HNO_3 solutions, then washed extraction of the organic phase 2 cycles by 4M 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 In) in high purity $ZrCl_4$ (repeat 3 times) were showed in table 5.

Table 5:- Levels of impurities in high purity $ZrCl_4$ after separation of the matrix Zr using 50% PC88A/kerosene.

Impurities	Levels (µg/g)	RSD (%)	Added (µg/g)	Total (µg/g)	Rev (%)
Li	11.868±0.539	4.5	2.5	14.248	95.2
B	14.358±0.864	6.0	2.5	16.741	95.3
			5.0	19.183	96.5
Na	5.154±0.178	3.5	2.5	7.597	97.7
			5.0	10.079	98.5
Mg	0.798±0.025	3.1	2.5	3.286	99.5
			5.0	5.828	100.6
K	12.632±0.786	6.2	5.0	17.767	102.7
Ca	2.035±0.061	3.0	2.5	4.610	103.0
			5.0	7.260	104.5
Sc	0.976±0.028	2.9	2.5	3.351	95.0
			5.0	5.791	96.3
Mn	6.659±0.237	3.6	2.5	9.172	100.5
			5.0	11.659	100.0
Co	1.546±0.061	3.9	2.5	4.096	102.0
			5.0	6.596	101.0
Cu	8.892±0.502	5.6	5.0	13.917	100.5
Ga	2.988±0.085	2.8	2.5	5.381	95.7
As	7.094±0.241	3.4	2.5	9.409	92.6
Se	0.278±0.008	2.9	2.5	2.603	93.0
			5.0	4.948	93.4
Sr	17.165±0.841	4.9	5.0	21.945	95.6
Y	0.219±0.007	3.2	2.5	2.602	95.3
			5.0	5.044	96.5
Mo	16.475±0.454	2.8	5.0	21.300	96.5
Ag	8.995±0.277	3.1	5.0	14.020	100.5
Cd	2.007±0.065	3.2	2.5	4.397	95.6
			5.0	6.807	96.0
Ba	22.769±0.743	3.3	5.0	27.519	95.0
La	4.103±0.242	5.9	5.0	8.883	95.6
Ce	4.003±0.167	4.2	5.0	9.068	101.3
Pr	2.632±0.076	2.9	5.0	7.682	101.0
Nd	1.346±0.033	2.5	2.5	3.729	95.3
			5.0	6.171	96.5
Sm	1.014±0.035	3.5	2.5	3.524	100.4
			5.0	6.114	102.0
Eu	0.561±0.023	4.1	2.5	3.099	101.5
			5.0	5.591	100.6
Gd	0.089±0.004	4.5	2.5	2.464	95.0
			5.0	4.859	95.4
Tb	0.115±0.005	4.3	2.5	2.498	95.3
			5.0	4.915	96.0

Dy	0.139±0.005	3.6	2.5 5.0	2.664 5.239	101.0 102.0
Ho	0.165±0.006	3.6	2.5 5.0	2.678 5.265	100.5 102.0
Er	0.331±0.009	2.7	2.5 5.0	2.744 5.156	95.6 96.5
Tm	0.134±0.006	4.5	2.5 5.0	2.677 5.234	101.7 102.0
Yb	0.152±0.006	3.9	2.5 5.0	2.715 5.252	102.5 102.0
Lu	0.075±0.004	5.3	2.5 5.0	2.465 4.900	95.6 96.4
Tl	1.015±0.032	3.2	2.5 5,0	3.398 5.800	95.3 95.7
Bi	0.538±0.025	4.6	2.5 5.0	2.923 5.303	95.4 95.3
Th	0.269±0.013	4.8	2.5 5.0	2.652 5.079	95.3 96.2
U	0.336±0.017	5.1	2.5 5.0	2.724 5.101	95.5 95.3

Table 5 shows that the levels of impurities in $ZrCl_4$ from 0.075 µg/g (Lu) to 22.769 µg/g (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 95.0 to 104.5% for different impurities. The %RSD of the methods varying between 2.5 and 5.9% 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 [14,15,16,17].

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 continued to the determination of impurities in zirconium materials of highly purity manufactured by Merck and NIST as ZrO_2, $ZrO(NO_3)_2$, Zircaloy-2, Zircaloy-4.

Conclusions:-

Capability strong extraction of Zr(IV) by PC88A were examined by infrared spectrum (IR) of $ZrO(NO_3)_2$, PC88A-kerosene and Zr-HNO_3-PC88A-kerosene. Effects of the concentrations of HNO_3 on the extraction efficiency of Zr(IV) and other elements by 50% PC88A/kerosene as the extractant. Results showed that in 3M HNO_3, the extraction efficiency of Zr(IV), Hf(IV) was very high and medium or very low with other elements. When extraction systems containing of 25 mg/mL Zr(IV) and 0.5 µg/L of each impurity by 50% PC88A diluents in kerosene, after 1 extraction from 3M HNO_3 and 1-2 cycles stripping by 4M HNO_3, more 95% of almost elements could be separated and Zr remaining in water phase is about 22-28%. 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 PC88A could be used for determination of impurities in materials of nuclear grade and high purity zirconium by ICP-MS. Direct determinable impurities results (using matching matrix and internal standard In) and after separation of the matrix Zr by 50% PC88A/kerosene (using standard addition) in high purity $ZrCl_4$ powders by ICP-MS. The values of RSD were less than 8.3% and Rev of 95.0 to 104.5% for both direct determination and after separation of the matrix Zr.

Acknowledgment:-

This work is supported in part by Project DH2016-TN04-05 of Thai Nguyen University. The authors expres their sincere thanks to Assoc. Prof. Le Ba Thuan, Head and Dr. Nguyen Xuan Chien, Diretor - Institute for Technology of

Radioactive and Rate Elements (ITRRE) for providing all the necessary facilities to complete the project and for their permission to publish this work.

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