INVESTIGATION OF DIRECT DETECTION OF MANY IMPURITIES IN HIGH PURITY ZrCl₄ 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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Abstract

ICP-MS using matching matrix and internal standard In is believed direct determination some impurities such as Al, Si, Ti, V, Cr, Fe, Ni, Zn, Nb, Mo, Sn, Hf, Ta and W in high purity ZrCl₄. 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(NO₃)₂, PC88A-kerosene and Zr-PC88A-kerosene. Impurities in ZrCl₄ were also determined 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 HNO₃ and 1-2 cycles stripping Zr and scrubbing impurities by 4M HNO₃, 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 determination 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 al. 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 determined 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 include 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-ethylhexylphosphoric acid (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:

\[
\begin{align*}
\text{CH}_3\text{(CH}_2\text{)}_3\text{CHCH}_2 & \quad \text{P} \quad \text{OH} \\
\text{C}_2\text{H}_5 & \\
\text{CH}_3\text{(CH}_2\text{)}_3\text{CHCH}_2\text{O} & \quad \text{O} \\
\text{C}_2\text{H}_5
\end{align*}
\]

In previous articles, the authors et al (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 ZrCl₄ sample was not studied. So, investigation of direct determination of many impurities in high purity ZrCl₄ 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 HNO₃ 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°C (Merck, Germany) were used as an extractant and diluents, respectively. All other reagents were analytical reagent grade of Merck company, Germany as: ZrCl₄ 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, Ti, Zn, Sc, Y, U, Th, 14 rare earth elements) 1000 µg/mL; Super pure HNO₃, HClO₄ 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 ZrCl₄ 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 HNO₃. The concentration of Zr(IV) in these solutions is 30 mg/mL.

Separation of Zr(IV) from HNO₃ media by PC88A/toluene solvent: -
Aqueous phase containing 25 mg/mL Zr(IV) and other impurities in 3M HNO₃ 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°C) unless stated otherwise. Separated aqueous phase and stripping of elements in organic phase from 1 to 2 cycles by 4M HNO₃ solutions. Merged aqueous phase and stripping solutions, added 5 mL of (25% HNO₃+ 20% HClO₄) solutions, evaporated to dryness and dissolved in 0.3M HNO₃ 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 ZrCl₄ 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 | 0.4 rps |
| Time pump (uptake) | 90s |
| Pump speed stability | 0.1 rps |
| Stable injection time (Stable) | 30s |
| Coolant | 2.4 L/min |
| Temperature spray chamber (S/C) and coolant | 20°C and 17°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 x 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 ZrCl₄ 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 ZrCl₄

| 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 ZrCl₄. 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 ZrCl₄ 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(NO₃)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(NO₃)₂, PC88A-kerosene and Zr-HNO₃-PC88A-kerosene. IR of the salt, solvent and the extracted complex showed on figure

(a) (b)
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) HNO₃ concentrations on the extraction efficiency of Zr(IV) and other elements with 50% PC88A/kerosene solvent
A - the extraction efficiency of Zr, Hf, Ti, 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 HNO₃ 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 HNO₃. The extraction efficiency of almost REEs was low (from 2.72 to 2.83%).

From stripping results of Zr(IV), we chose 4M HNO₃ 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 HNO₃. 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 HNO₃ and 1 stripping by 4M HNO₃ using 50% PC88A/kerosene

| Elements | Aqueous phase, % | Organic phase, % |
|----------|-----------------|------------------|
| Li, Na, K, Rb, Mg, Ca, Sr, Ba, Al, Ga, Ti, 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 | ≈100 | Not detected |
| Tm, Yb, Lu | 89 | 11 |
| Ti | 94 | 06 |
| Fe | 62 | 38 |
| Hf | 28 | 72 |
| Zr | 22 | 78 |

Table 4: Contented of elements in aqueous phase and organic phase after 1 extraction by 3M HNO₃ and 2 cycles stripping by 4M HNO₃ using 50% PC88A/kerosene

| Elements | Aqueous phase, % | Organic phase, % |
|----------|-----------------|------------------|
| Li, B, Na, K, Rb, Mg, Ca, Sr, Ba, Al, Ga, Ti, 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 | ≈ 100 | Not detected |
| Tm, Yb, Lu | 95 | 05 |
| Y | 98 | 02 |
| Ti | 70 | 30 |
| Fe | 35 | 65 |
| Hf | 28 | 72 |

Tables 3 and 4 were detected after 1 extraction by 3M and 1 to 2 cycles stripping by 4M HNO₃ solutions, the recoveries were found as 95-100% so that 21 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   |
| Na         | 5.154±0.178  | 3.5     | 5.0          | 10.178       | 97.7   |
| Mg         | 0.798±0.025  | 3.1     | 5.0          | 5.828        | 98.5   |
| K          | 12.632±0.786 | 6.2     | 5.0          | 17.767       | 102.7  |
| Ca         | 2.035±0.061  | 3.0     | 5.0          | 7.260        | 104.5  |
| Sc         | 0.976±0.028  | 2.9     | 5.0          | 5.791        | 96.3   |
| Mn         | 6.659±0.237  | 3.6     | 5.0          | 11.659       | 100.0  |
| Co         | 1.546±0.061  | 3.9     | 5.0          | 4.948        | 93.4   |
| Cu         | 8.892±0.502  | 5.6     | 5.0          | 13.917       | 100.5  |
| Ga         | 2.988±0.085  | 2.8     | 5.0          | 5.381        | 95.7   |
| As         | 7.094±0.241  | 3.4     | 5.0          | 9.409        | 92.6   |
| Se         | 0.278±0.008  | 2.9     | 5.0          | 4.948        | 93.0   |
| 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   |
| 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     | 5.0          | 4.857        | 95.6   |
| 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     | 5.0          | 3.729        | 95.3   |
| Sm         | 1.014±0.035  | 3.5     | 5.0          | 6.114        | 100.4  |
| Eu         | 0.561±0.023  | 4.1     | 5.0          | 3.099        | 101.5  |
| Gd         | 0.089±0.004  | 4.5     | 5.0          | 2.464        | 95.0   |
| Tb         | 0.115±0.005  | 4.3     | 5.0          | 2.498        | 95.3   |
|   |   | 0.139±0.005 | 3.6 | 2.5 | 2.664 | 5.0 | 5.239 | 101.0 | 102.0 |
|---|---|-------------|-----|-----|-------|-----|-------|-------|-------|
| Dy |   | 0.165±0.006 | 3.6 | 2.5 | 2.678 | 5.0 | 5.265 | 100.5 | 102.0 |
| Ho |   | 0.331±0.009 | 2.7 | 2.5 | 2.744 | 5.0 | 5.156 | 95.6  | 96.5  |
| Er |   | 0.134±0.006 | 4.5 | 2.5 | 2.677 | 5.0 | 5.234 | 101.7 | 102.0 |
| Tm |   | 0.152±0.006 | 3.9 | 2.5 | 2.715 | 5.0 | 5.252 | 102.5 | 102.0 |
| Yb |   | 0.075±0.004 | 5.3 | 2.5 | 2.465 | 5.0 | 4.900 | 95.6  | 96.4  |
| Lu |   | 1.015±0.032 | 3.2 | 2.5 | 3.398 | 5.0 | 5.800 | 95.3  | 95.7  |
| Tl |   | 0.538±0.025 | 4.6 | 2.5 | 2.923 | 5.0 | 5.303 | 95.4  | 95.3  |
| Bi |   | 0.269±0.013 | 4.8 | 2.5 | 2.652 | 5.0 | 5.079 | 95.3  | 96.2  |
| Th |   | 0.336±0.017 | 5.1 | 2.5 | 2.724 | 5.0 | 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.

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