

# Chemical Analysis of High-Level Nuclear Waste Elements Fixed in Sodium Zirconium Phosphate ( $\text{NaZr}_2\text{P}_3\text{O}_{12}$ ) Matrix

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## Abstract

High-level nuclear waste such as Caesium (Cs), Strontium (Sr), Tellurium (Te) and Ruthenium (Ru) was fixed in sodium zirconium phosphate (NZP) at very low temperature by adopting microwave synthesis. The quantity of substituted elements in the matrix was confirmed by dissolving doped NZP in a mixture of acids along with fusion mixture at 1073 K. The results obtained are not satisfactory for the elements like Cs and Te which are considerably volatile at this temperature. Hence microwave digestion method was adapted to obtain comparative data. Quantitative analysis of the solution was done by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Results acquired revealed that microwave dissolution method gives more accurate and appropriate result compare to conventional dissolution method.

This work describes not only fixation of elements in the matrix but also detection of the exact amount of element that got fixed in the NZP ceramic, which will open the new path in the field of the fixation of nuclear waste in the ceramic matrix.

**Keywords:** Sodium zirconium phosphate; Microwave heating; Fusion mixture; ICP-MS

## Introduction

Several environment-friendly options are being considered to face the impounding energy crisis resulting due to depletion of conventional fossil fuels. Among these, nuclear energy emerges as the most viable alternative. There are no major gaseous emissions during the production of electrical energy from nuclear fuel, which will contribute to global warming and toxicity.

The nuclear power generation is accompanied by the formation of highly radioactive waste, which should not be allowed to mix up with the environment, therefore the most important aspect of nuclear power generation is to immobilize this waste containing highly radioactive elements using suitable procedures and dispose of it safely in repositories far away from human habitation. Currently, these wastes are obtained in the form of nitrate, after reprocessing of this irradiated fuel, which on further heating produces a mixture of oxides, then they are incorporated in the glass matrix by heating the charge to the pouring temperature of glass which is about 1373 K [1]. During this process, oxides of several elements such as those of Cs, Ru, Te etc., vaporize and get deposited in the ducts and pipelines connected to the processing plant making this area inaccessible for working technicians, due to high radioactivity matrix at low temperatures where the vaporization of these oxides is not significant.

The other disadvantage of fixing the radioactivity in the glass is mainly due to its thermodynamic meta-stability. The solidified glass contained in the canisters located in the repositories can spontaneously de-vitrify and results in liberation of a large amount of energy and

breaching of canisters due to thermal expansion of the solid glass matrix during transformation, thereby exposing the radioactivity to the environment.

Several options have been proposed for the fixation of high-level nuclear waste, as a viable alternative to glass, which is currently used [2]. Numbers of ceramic waste forms have been identified and their potentials have been indicated for the fixation of high-level nuclear waste [3]. Ringwood et al. [4] proposed the material named SYNROC which is composed of a mixture of three to six different phases tailored to immobilize specific radioactive cations. This was followed by sodium zirconium phosphate (NZP),  $\text{NaZr}_2\text{P}_3\text{O}_{12}$ , which was first reported as potential host for nuclear waste by Roy et al. [5], Scheetz et al. [6] in their review presented some data on the fixation of simulated waste and its subsequent leaching behavior from sodium zirconium phosphate. Their conclusions indicated that NZP could be the most suitable candidate for the replacement of glass for fixing high-level nuclear waste. They surmised that unlike in SYNROC, almost all the fission products can be incorporated in a single NZP phase owing to its peculiar structure.

In our preceding publication [7-10] we have depicted how to design suitable method using thermal analysis techniques and prepare highly pure NZP at as low as 723 K by microwave irradiation [11]. At the same temperature selected elements (Cs, Sr, Te, and Ru) from high-level nuclear waste were substituted in NZP matrix [12] After the fixation of elements in the matrix, there is need to estimate the amount of element retained in the matrix, as it is well known that the microwave heating is at the molecular level and different for the different elements. Therefore there is the probability of evaporation of some elements even at such a low temperature. In order to verify this, we have developed a suitable method to estimate the exact amount of

doped elements in the matrix. Investigation portrayed in this paper is unfolding suitable method to estimate the number of elements substituted in the NZP matrix.

## Materials and Methods

### Instrumentation

A VG Plasma Quad PQ II (V.G.Elemental, Winsford, Cheshire, England) ICP-MS was used for the determination of a doped element in NZP matrix. Sample introduction was carried out by pneumatic nebulization using a Meinhard concentric nebulizer, a double-pass Scott-type spray chamber cooled to 283 K with a locally made recirculating chiller, and a Fassel-type torch. The solution flow rate was controlled by a peristaltic pump (sample uptake rate: 1 mL min<sup>-1</sup>). The ICP-QMS conditions were optimized daily for maximum sensitivity and calibrated using a 100mg.mL<sup>-1</sup> tuning solution of Cs, Sr, Te, and Ru. A quadrupole mass analyzer having a mass range of 1–300 amu with a resolution of 0.3 amu has been employed. The optimum operating conditions of the instrument are given in Table 1.

Nebulizer Meinhard (concentric)	Spray Chamber Double-Pass Scott-Type
RF Power 1150 W	Frequency 27.12 MHz
Cool Gas Flow Rate 18 L min <sup>-1</sup>	Auxiliary Gas Flow Rate 0.8 L min <sup>-1</sup>
Nebulizer Gas Flow Rate 1.0 L min <sup>-1</sup>	Sample Uptake Rate 1.0 mL min <sup>-1</sup>
Detector Mode Dual (PC/Analog)	Integration Time 10 ms

**Table 1:** Operating conditions of ICP-MS.

### Reagents and solutions

High purity reagents were used for the preparation of the standards, and all solutions were prepared in de-ionized water obtained from a Milli-Q™ system (18 MΩ, Millipore, Bedford, MA, USA). Stock solutions of doped NZP were diluted daily to obtain the working solutions. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1 mol L<sup>-1</sup> HNO<sub>3</sub> (65% Suprapur® E. Merck, Darmstadt, Germany). Instrument calibration standard solutions of diverse elements were prepared by dilutions from 1000 mg L<sup>-1</sup> stock solutions (BDH, Leicestershire, UK).

### Preparation of doped NZP

Each of the selected fission product in the form of either carbonate or oxide was mixed with appropriate amount of stoichiometric mixture of Na<sub>2</sub>CO<sub>3</sub>, Zr(NO<sub>3</sub>)<sub>2</sub>. 5H<sub>2</sub>O and NH<sub>3</sub>H<sub>2</sub>PO<sub>4</sub> individually to yield 2% of a dopant. When added in combination, Cs<sub>2</sub>O and SrCO<sub>3</sub> were added to yield 1% of respective elements, whereas TeO<sub>2</sub> and RuO<sub>2</sub> were added to yield the stoichiometric amount of Te and Ru with respect to Cs and Sr so that they can form thermodynamically stable metal tellurite or ruthenate. The percentage calculation for Cs and Sr is with respect sodium, while for Te and Ru it was with respect to Zr in NZP matrix. The detailed procedure of preparation of doped NZP is described elsewhere [13].

### Estimation of the substituted elements in the matrix by ICP-MS

**Dissolution of doped NZP by a fusion method:** 0.1 g of doped NZP prepared at 723 K was mixed thoroughly with 600 mg of fusion mixture (equimolar mixture of potassium and sodium carbonate) and heated in a platinum crucible using muffled furnace at 1073 K for 1 h. The heated mixture was allowed to attain room temperature naturally and then dissolved in minimum amount of conc. HCl. A semitransparent solution was obtained, which became transparent when few drops of HF were added. HCl and HF in the solution were evaporated by heating on a hotplate. Concentrated HNO<sub>3</sub> was added constantly during the process so that the solution will not turn dry. On the complete evolution of HCl the solution obtained is concentrated to minimum volume and diluted to 100 ml by adding 1% nitric acid, this solution was used as stock for further analysis. 0.5 ml of this solution was diluted to 100ml and used for the estimation of the different element by ICP-MS, when running along with the standards of 100, 200 and 500 ppb. A similar procedure was followed during the estimation of elements in all other samples. Each sample was run at least four times and the values obtained were found to be within ± 5% variation. The results calculated from the average value of all four readings of each sample are presented in Table 2. Except for Te and Cs, the concentration of all other elements was in close agreement with the amount added in the NZP matrix.

Doping combination	Element	Amount added (mg)	Amount estimated (mg)
Cs	Cs	12.19	4.31
Sr	Sr	8.95	9.76
Te	Te	12.66	9.2
Ru	Ru	9.23	9.2
Sr-Cs	Sr	4.5	5.17
	Cs	6.1	1.62
Sr-Ru	Sr	4.5	4
	Ru	4.62	4.63
Sr-Te	Sr	4.03	4.7
	Te	5.88	6.14
Sr-Cs-Te	Sr	4.5	3.78
	Cs	6.1	1.02
	Te	11.77	8.15
Sr-Cs-Ru	Sr	4.5	5.6
	Cs	6.1	0.7
	Ru	9.23	9.3

**Table 2:** Amount of doped element in NZP estimated by conventional fusion route.

**Dissolution of doped NZP using microwave digestion system:** However, to ascertain the evaporation of doped element at fusion temperature, dissolution procedures using a Multiwave® 3000 microwave (Anton Paar, Austria) was adopted. In each case, 0.1 g of

doped NZP sample was dissolved in a combination of 2 ml conc. HCl and 0.1 ml HF. The solution was evaporated by heating on a hot plate. Concentrated HNO<sub>3</sub> was added constantly during the process so that the solution will not turn dry. On the complete evolution of HCl the solution obtained is concentrated to minimum volume and diluted to 100 ml by adding 1% nitric acid, this solution was used as stock during further analysis. The operating parameters of the microwave digestion are given in Table 1. 0.5 ml of this solution was diluted to 100ml and used for the estimation as a sample solution. This was followed by quantitative measurements by ICP-MS with an external calibration standard.

## Results and Discussion

The Table 2 shows the number of elements substituted in the NZP matrix at the time of synthesis and the value obtained from ICP-MS investigation estimated by conventional route. The following conclusion can be drawn from Table 2.

1. Among all the elements Sr and Ru were retained completely whereas Te and Cs deviated considerably from quantity added when incorporated individually in the NZP matrix.

2. Addition of Sr in combination with Ru or Te (Sr-Te and Sr-Ru), both the elements were retained completely, but on the inclusion of third element Cs some loss in weight was observed in the mass of Sr and Te in Sr-Cs-Te sample.

3. When Te was added alone, some loss was observed. This loss may be due to vaporization of Te at the preparation temperature or during the dissolution of the matrix by fusion method. But when it was added in combination with strontium, it was retained completely. This can be attributed to the formation of thermodynamically stable compound strontium tellurite [14].

4. Similarly, Ru was retained completely when added simultaneously with the Sr, this may be due to the formation of stable compound strontium ruthenate [15]. It was also retained quantitatively when added individually.

5. From the above Table 2, it was found that cesium estimated for all samples was always less than, the amount of cesium added during preparation; this may be due to the addition of a non-stoichiometric amount of cesium or may be due to vaporization of cesium during preparation or during the dissolution of the matrix by fusion method.

Since Cs was added to reactant mixture in the form of cesium oxide (Cs<sub>2</sub>O) and tellurium in the form of TeO<sub>2</sub>, which are highly stable at room temperature, hence the probability of addition of these elements in non-stoichiometry is eliminated. Also, NZP is prepared at as low as temperature 723 K by microwave irradiation, hence the possibility of vaporization of cesium and tellurium at such a low temperature was considered to be negligible. Therefore it was sure that the vaporization of the Cs and Te is during dissolution process of the substituted NZP matrix. On the variation of fusion temperature, the amount of Cs and Te in the same sample was found to be different. Hence to confirm this fact we decided to analyze all the samples containing Cs and Te elements by another route. The challenge was to dissolve the matrix material at a lower temperature.

These days, microwave synthesis is fetching more popularity in material science. Microwave irradiation is highly beneficial for a solid-state reaction because, in the microwave, materials are heated uniformly at a molecular level compared to conventional heating

where the sample is heated from outer surface to the interior and thus resulting steep thermal gradient. In our work itself, we found that the microwave can lower down the temperature of reaction [16]. Hence we decided to use microwave digestion system to dissolve substituted NZP matrix.

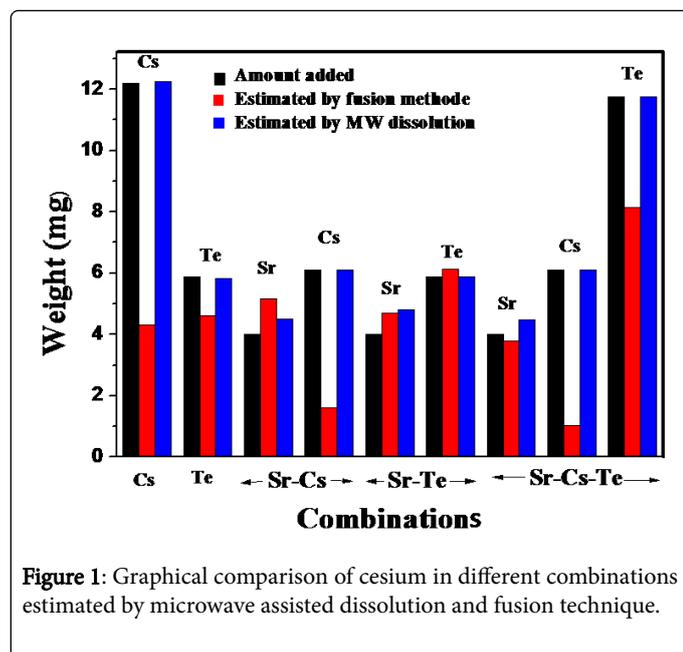
## Estimation of Cs and Te in the substituted NZP matrix

**Estimation of cesium (Cs) in the matrix:** Hence, all the samples containing Cs were dissolved using microwave digestion system. Since microwave dissolution was carried out at as low as 433 K, the possibility of loss of cesium during dissolution was minimal. It was found that the quantities of Cs added and values obtained from microwave dissolution for cesium containing samples were in close agreement (Table 3).

Doping combination	Element	Amount added (mg)	The amount estimated by a fusion method (mg)	The amount estimated by MW dissolution (mg)
Cs	Cs	12.19	4.31	12.25
Te	Te	5.88	4.6	5.83
Sr- Cs	Sr	4.02	5.17	4.5
	Cs	6.1	1.62	6.11
Sr- Te	Sr	4.02	4.7	4.8
	Te	5.88	6.14	5.88
Sr-Cs-Te	Sr	4.02	3.78	4.47
	Cs	6.1	1.02	6.1
	Te	11.77	8.15	11.76

**Table 3:** Amount of the elements in the doped NZP estimated by microwave dissolution and by fusion method.

The analysis of Cs carried out by microwave dissolution of sample clearly indicates that the loss of Cs in the sample was due to vaporization of Cs at the time of fusion of substituted matrix with fusion mixture and not during preparation. The amount of Cs in Cs-Sr-Ru sample is not estimated since Ru-containing samples didn't dissolve even when these were heated for more than 3h in microwave digestion system. Figure 1 shows the graphical comparison of the Cs estimated in all the samples by different dissolution methods.



**Figure 1:** Graphical comparison of cesium in different combinations estimated by microwave assisted dissolution and fusion technique.

**Estimation of tellurium (Te) in the matrix:** The possibility of losing Te during fusion was confirmed by dissolving the samples in a mixture of conc. HCl and HF (5:1) by microwave dissolution. The results obtained show good agreement with the amount of Te and other elements added, with those estimated by microwave digestion dissolution method. The data are presented in Table 3. It was also observed that when Te was added along with Sr it was retained completely.

Thus the dissolution of substituted NZP matrix by fusion method to estimate the amount of element is suitable only for those elements whose vaporization temperature is less than fusion temperature, for volatile elements the results are misleading. Microwave digestion dissolution is showing excellent results with a very good agreement with the number of elements added to the NZP matrix. This method will help other researchers to select a suitable method for dissolution of phosphate material in quantitative analysis of trace level elements in the matrix.

Many researchers try to fix high-level nuclear waste in a different ceramic matrix such as NZP, SYNROC etc. [4-6,17] and studied the rate of leaching of the substituted elements in the different conditions. But, nobody has reported the exact amount of elements got fixed in the matrix. This work describes not only fixation of elements in the matrix but also detection of the exact amount of element got fixed in the NZP ceramic, which will be open, the new path in the field of fixation of nuclear waste in the ceramic matrix.

## Conclusion

The quantitative estimation of doped elements in ceramic by the implementation of conventional dissolution method gives misleading

results due to vaporization of highly volatile elements such as cesium, tellurium etc. The microwave dissolution technique revealed that the loss of volatile element from matrix was during fusion of matrix at a higher temperature. Hence microwave dissolution method is the most suitable method for quantitative estimation of volatile elements doped in a ceramic matrix such as NZP.

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