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Laser mass spectrometric studies on rare earth doped UO_2

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Abstract

A laser mass spectrometry system comprising of in-house developed reflectron time-of-flight mass spectrometer was used to study solid and liquid samples containing UO_2 doped with lighter rare earths (La, Ce, Sm and Nd). Unit mass resolution is obtained for all the rare earth isotopes. Preliminary results indicate that this method has potential for direct determination of burnup of irradiated nuclear fuel.

Keywords: Laser mass spectrometer; Rare earth doped UO_2

1. Introduction

Post-irradiation examination of nuclear fuel is necessary to evaluate the fuel performance, fuel clad interaction, burnup, fission products and their spatial distribution, fissile atoms distribution, etc. Among these, burnup is very important parameter. Conventional wet chemical methods of determination of burnup involve very elaborate and time consuming procedures, leading to separation of uranium, plutonium and the rare earths group fractions, followed by separation of the individual rare earth elements. Isotope dilution studies using thermal ionization mass spectrometry (TIMS) are then used for the determination of the above separated elements [1,2]. In particular the separation of pure neodymium fraction from the rare earths group by conventional ion-exchange chromatography is time consuming. Earlier we had reported the use of high performance liquid chromatography (HPLC) for the rapid separation of lighter rare earths, which are potential burnup monitors [3]. However, this method needs separation of rare earths group from the irradiated, dissolved fuel solution prior to injection into HPLC columns [4]. A direct method of determination of burnup of an irradiated pellet will dispense with labor-intensive separation procedures but will involve handling of highly radioactive solid samples in a hot cell. Also, such a method needs to be highly quantitative. Though such quantitative estimation has been reported using laser mass spectrometry (LMS) method for solid samples [5], it would be preferable to use the relative ion signal intensities, rather than absolute intensities as there will be pulse to pulse fluctuations in the laser pulse energy and the sample surface morphology can be different for one pulse to another. The difference in the signal intensities that arise from pulse to pulse due to changing surface morphology seem to be reduced by the use of thin layer (films) prepared from a small volume of sample solutions dried under an infrared lamp. But drying the solution to a solid film has other important advantages, namely,

(i) one needs to use a small volume (~10 μL) of the solution as opposed to use of the sample pellet thereby reducing the radioactivity to be handled significantly and
(ii) one can easily perform isotope dilution (as in TIMS) or addition of internal standards [6], to ensure desired accuracy.

We present results that indicate that laser mass spectrometry on thin film of samples prepared from solutions of small volume (~10 μL) can provide the desired direct determination of burnup without the need for chemical separations.

2. Experiment

Schematic of the LMS facility developed in our laboratory is shown in Fig. 1. A Q-switched Nd:YAG laser (M/s Continuum Model NY/61, USA) was used. The 1064 nm (fundamental) beam of 8 ns pulse duration and mostly TEM_{00} mode was used to transiently heat the sample. The repetition rate was 10 Hz. A reflectron time-of-flight mass spectrometer (RTOFMS) of

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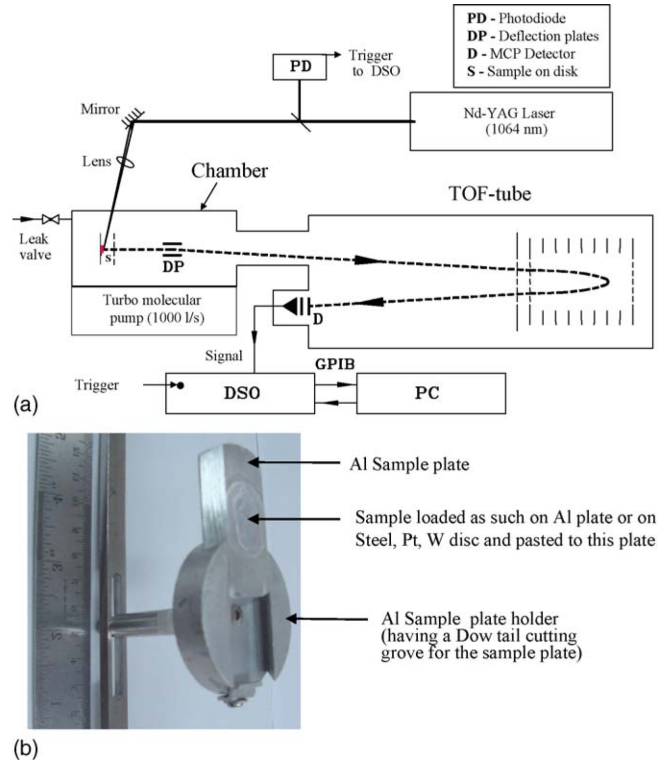

Fig. 1. (a) Schematic of the experimental facility; (b) photograph of the sample holder.

Mamyrin type [7], built in our laboratory, was used for mass analysis of the ions produced from the heated surface. A quartz lens with a focal length of 25 cm was used for focusing the laser beam and the target was positioned after the focus. The power density incident on the sample surface was varied by changing the distance from lens to the sample surface. A micro channel plate (MCP) was used as the detector. The signal from the detector was amplified by a fast pre-amplifier (Philips Scientific Model 6950) and fed to a digital storage oscilloscope (DSO, LeCroy, Model 9350AM). The DSO was triggered by the signal from a photodiode as indicated in Fig. 1a. The mass spectrum was obtained by summation averaging the signal for 1000 laser shots. The thin film made from dried sample solution on a metallic plate (steel, platinum, tungsten, etc.), applied as a drop of a few microliters, was positioned by an aluminum holder (marked as S in Fig. 1a and b). Solid samples (∼2 mm thick pellets) are directly pasted on the aluminum plate using silver paint. A base pressure below 1×10^{-6} Torr was maintained by a turbo molecular pump (1000 L/s), in the vacuum chamber containing the sample and the mass spectrometer. The typical mass resolution of our instrument is about 1000, comparable to any commercial instrument as determined using laser ionization of I_2 in the gas phase [8]. In the present experiments, the ion flight energy was kept at 1000 eV.

2.1. Solid samples

The solid samples of lighter rare earths (La, Ce, Sm and Nd) doped UO_2 was prepared by the combustion synthesis method. U_3O_8 (nuclear grade), CeO_2, La_2O_3, Sm_2O_3 and Nd_2O_3 (all rare earths are of 99.9% pure, from M/s Indian Rare Earths) were used as the starting materials. The U:RE (rare earth) element ratio is taken in the range corresponding to an approximate burnup of 10 at.% fission to 25 at.% fission in UO_2 matrix as calculated for a mixed oxide fuel (MOX) used in a fast reactor [9]. The nitrates of these elements were prepared by dissolution of their oxides in analytical grade nitric acid (in the case of CeO_2, HF was added to enable dissolution). These solutions were dried by evaporation on hot plate. Aqueous solutions of these nitrates were mixed with the required amount of citric acid and the resultant solution was heated to 450 °C for 5 h in air using a resistively heated furnace. The resulting powder was heated in reducing atmosphere at 1000 °C for 8 h. This powder was then pelletized and sintered at 1400 °C for 6 h. The thus made pellets were used as solid samples for the LMS studies.

2.2. Thin film samples prepared from solutions

Standard solutions were prepared for rare earths and U from the respective nitrate solutions. Appropriate volume of these solutions were taken and mixed to have the desired rare earth to U ratio. From these sample solutions a small volume, ∼100 μL was added to tri-butyl phosphate (TBP) in methanol. The ratio of number of moles of TBP to the number of moles of metal in the solution was 3:1. TBP is used here as the matrix for efficient laser desorption and ionization, as reported in the literature [10]. From these sample solutions ∼10 μL was applied as a drop on metallic substrates, such as Pt, Al, W and steel; the typical area of the dried sample is ∼50 mm^2.

3. Results and discussion

Fig. 2 shows a typical mass spectrum obtained for a film prepared from the solution sample of neodymium nitrate in TBP and methanol on a steel substrate. The time-to-mass calibration is done based on the standard procedure [11]. Larger signal intensities were observed for the steel substrates compared to other

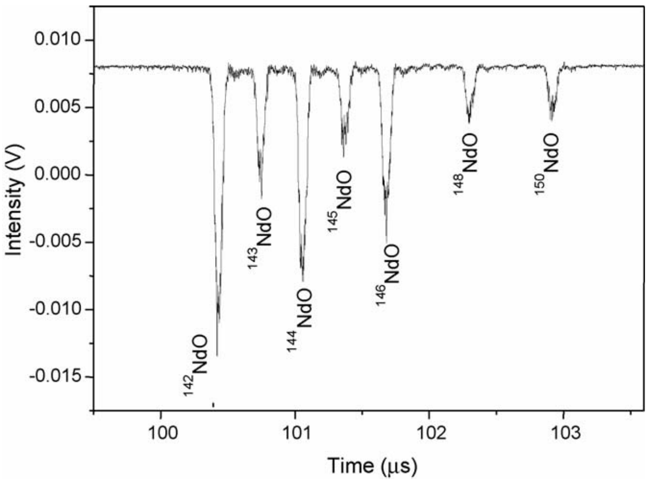

Fig. 2. Typical mass spectrum of Nd isotopes obtained from a sample of $Nd(NO_3)_3$ in TPB and methanol matrix.

metal substrates such as Pt, Al and W. This may be attributed to the better absorption of 1064 nm laser beam by steel compared to other metals used. Mass spectra with good resolution containing only oxide ions were observed when the laser power density is low (~1×10^7 W/cm^2). On increasing the incident laser power density, the intensity of the oxide ions decreases while the elemental ion intensity started increasing. At higher power densities, the mass resolution obtained was poor because of larger spread of initial energy of the ions as they come off the surface. Therefore, in all our experiments the incident laser power density was optimized to have only oxide ions in the mass spectrum. Table 1 compares the isotope ratios obtained for natural Nd with values reported in the literature.

Fig. 3a shows a typical mass spectrum of a film prepared from a sample solution containing La, Ce, Nd, Sm and UO_2 with added TBP and methanol. The iron oxide species observed are the desorption/ionization peaks from the substrate as confirmed by the spectra for the bare substrate. When the laser is loosely focused, it is possible that the laser beam could fall on the substrate as well. The composition of the sample solution is given in the figure. Even though the sample loaded on the metal plate is large, the amount of sample removed per pulse is expected to be of the order of picomoles [12]. Fig. 3b shows expanded view of the mass spectrum containing the rare earths ions. As can be seen from these figures, all isotopes of the lighter rare earths are well resolved. Keeping in view of the possible burnup monitors (^{143}Nd, ^{146}Nd and ^{139}La) of natural U and Pu mixed oxide fuel for a fast breeder reactor (FBR), the variation of ion signal intensities for these isotopes and that of UO_2^+ with the number of laser pulses that were incident on the sample film is plotted in Fig. 4. The signal intensities decrease by a factor of two within 10,000 laser pulses. This was observed for solid samples (of ≈70% of its theoretical density) as well. Rastering of the sample may provide more steady intensities [13], but in the present experiments this feature was not available. Even though, the absolute intensity levels are reduced to a large extent, the ratio of intensities of RE elements to that of UO_2 remains nearly constant as can be seen in Fig. 5. In order to use these isotopes of Nd for burnup determination, the intensity ratio of ^{143}NdO/^{146}NdO must remain constant for any composition of U:Nd ratio in the natural sample. Fig. 6 gives the obtained values for composition of U:Nd in the range from 16:1 to 242:1. As can be seen, the obtained value is always higher than the value expected for natu-

Table 1
Comparison of isotopic abundance of natural Nd as measured by LMS method with that of literature values [18]

Isotopes of Nd	Observed (at.%)	Literature value (at.%)
^{142}Nd	27.27 ± 0.54	27.13
^{143}Nd	12.55 ± 0.38	12.18
^{144}Nd	23.46 ± 0.50	23.8
^{145}Nd	8.48 ± 0.32	8.3
^{146}Nd	17.08 ± 0.32	17.19
^{148}Nd	5.73 ± 0.27	5.76
^{150}Nd	5.48 ± 0.23	5.64

The range is one standard deviation.

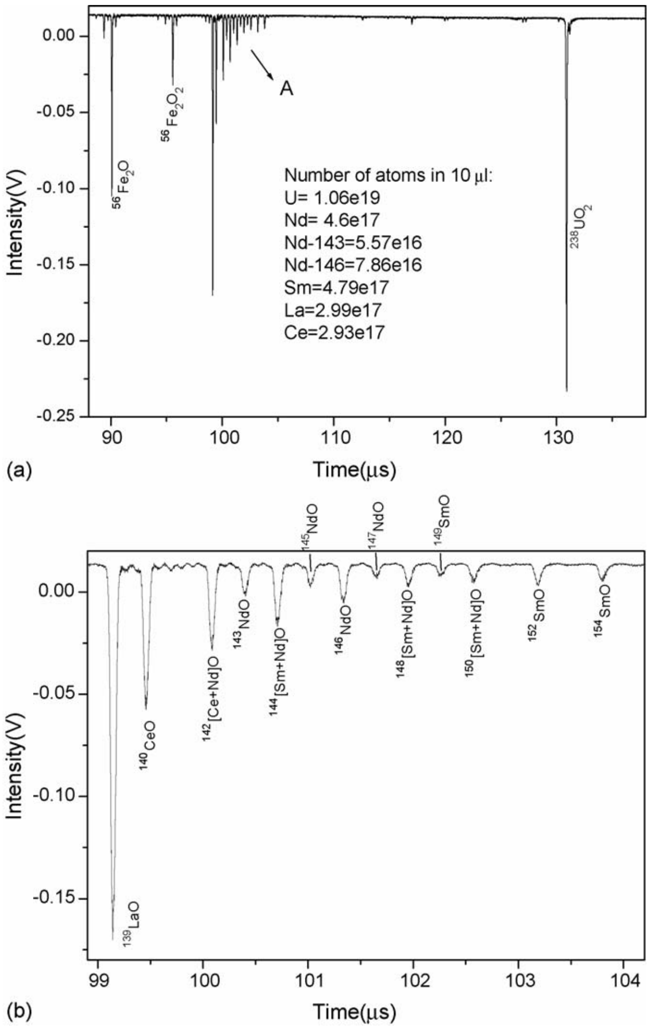

Fig. 3. (a) Typical mass spectrum of U, La, Ce, Nd and Sm in TBP/methanol mixture; sample loaded on steel disc; (b) mass spectrum corresponding to the region A of (a).

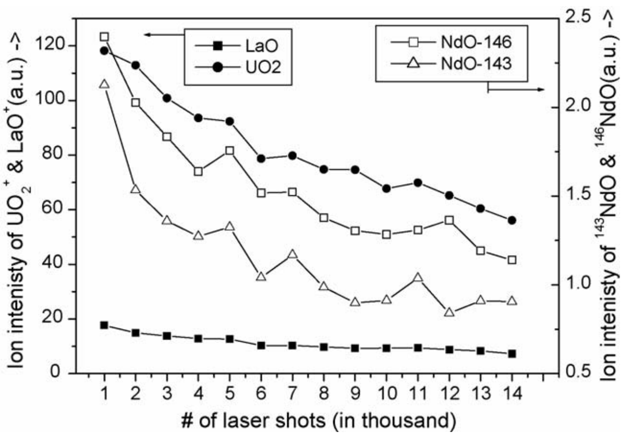

Fig. 4. Variation of intensity of ^{139}LaO$^+$, ^{143}NdO$^+$, ^{146}NdO$^+$, UO_2^+ as a function of laser shots on a solution sample.

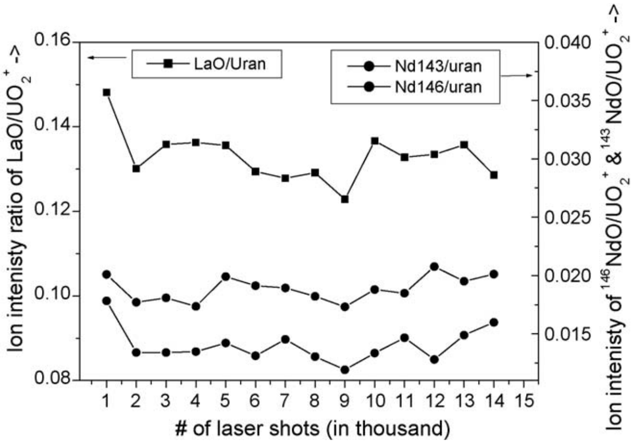

Fig. 5. Variation of intensity ratios of $^{139}LaO^+$, $^{143}NdO^+$, $^{146}NdO^+$ with respect to $UO_2{}^+$ as a function of laser shots on liquid sample.

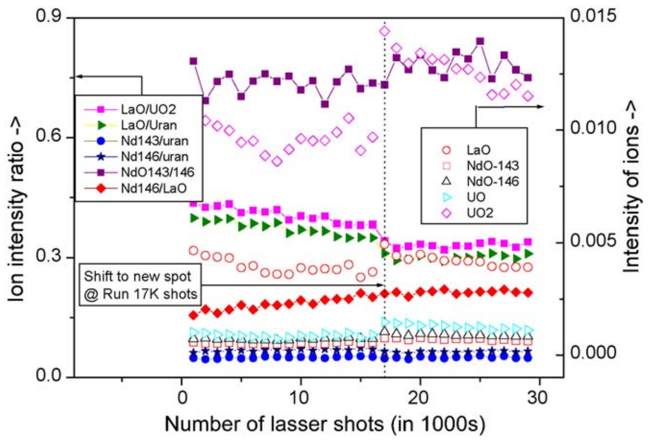

Fig. 7. Variation of ion intensities of $^{139}LaO^+$, $^{143}NdO^+$, $^{146}NdO^+$, UO^+ and $UO_2{}^+$; also their ratios with respect to uranium species as a function of laser shots for a solid sample pellet.

ral abundance. The extent of uncertainty increases for sampling smaller Nd fraction. We do not quite understand the reasons for this. Earlier, similar non-linear behavior was observed in the analysis of boron isotope ratio measurements [14]. Based on our experience on boron isotope measurements and the present results, we can attribute this increase in uncertainty to nonlinear gain of the MCP detector, when a very large number of ions hit the MCP detector. Using laser desorption–ionization method, as being used in the present experiment, it is very difficult to control the number of ions formed for each laser pulse. However, this type of non-linear behavior in MCP detector can be overcome by using fast rise time secondary electron multiplier (SEM) instead. The decrease in the ion signal intensities with the number of incident laser pulses is less for solid samples compared to solution samples. The surface morphology of the solid samples play a role because the signal intensities are observed to increase if the laser focus is moved to another point on the sample and also the ratios do not remain constant however, as can be seen in Fig. 7. Therefore, for burnup measurements it would be preferable to use solution samples. Also, the mass resolution obtained with solution samples is better than that obtained for solid samples (in the form of pellets). Though the reason for this is not immediately clear, it must arise due to a different spread in initial ion energies for the two cases.

As the absolute ion intensities vary with the number of incident laser pulses, intensities ratio of the rare earth oxides (REO)/UO_2 obtained is considered against the actual RE/U present in the solution sample composition and are presented for ^{139}La, ^{143}Nd and ^{146}Nd in Figs. 8–10. These figures do not evidence a good linear correlation. We believe that improvements can be made by: (i) rastering of the sample, instead of irradiating the same sample spot or identifying a suitable liquid matrix which can replenish the sample during the laser irradiation, or use of porous solid matrix, such as porous Si [15]; (ii) use a laser which has highly stable pulse energy (by using a photo detector to control the laser irradiation intensity); (iii) using a pulsed ion beam to desorb the species from the liquid sample, followed by

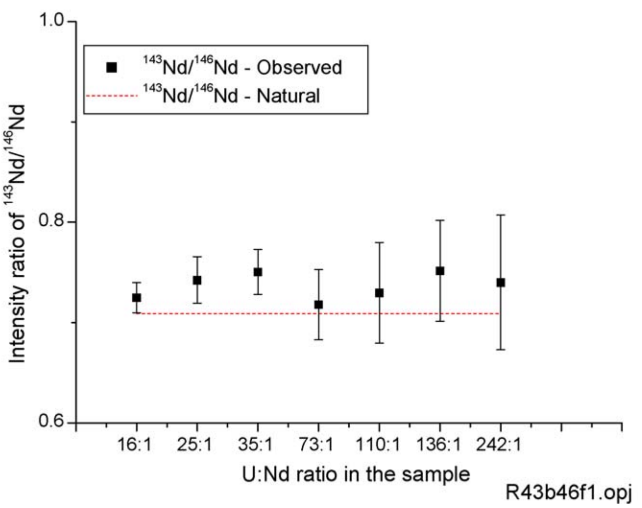

Fig. 6. Observed intensity ratio of $^{143}NdO^+/^{146}NdO^+$ against the different sample compositions.

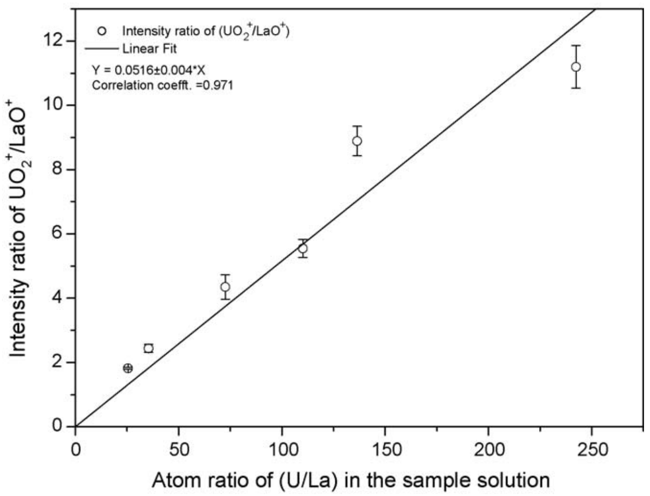

Fig. 8. Calibration plot of intensity ratio of $UO_2{}^+/LaO^+$ against the ratio of actual number of atoms present in the solution samples.

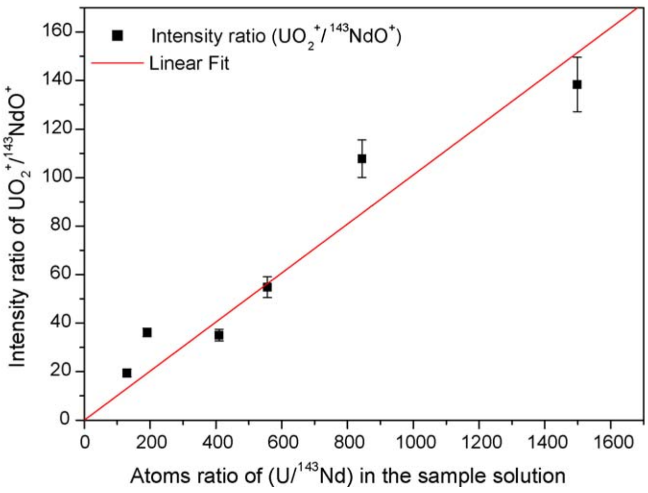

Fig. 9. Calibration plot of intensity ratio of $UO_2^+/^{143}NdO^+$ against the ratio of actual number of atoms present in the solution samples.

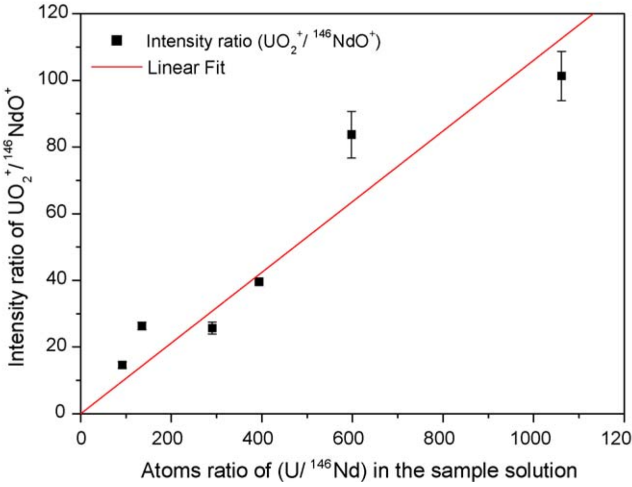

Fig. 10. Calibration plot of intensity ratio of $UO_2^+/^{146}NdO^+$ against the ratio of actual number of atoms present in the solution samples.

laser ionization; (iv) possibly applying suitable correction factor for the non-liner behavior of the MCP detectors or use of fast SEM. Our present experimental facility does not have the stated provisions and the efforts are underway to incorporate some of the above features.

4. Burnup computation

Using the ratio of signal intensity of the rare earth oxide ion to that of the heavy elements, one can determine the burnup based on the following procedure. Generally, burnup is determined by the use of the following equation [16]

$$\text{Burnup (at.\% fission)} = \frac{A/Y}{H + (A/Y)} \times 100$$

where A is the number of atoms of fission product monitor, Y the fractional fission yield and H is the total number of residual heavy atoms. The present method measures only the ratio A/H, i.e., the ratio of (number of atoms of burnup monitor)/(number of atoms of heavy atoms), and the burnup can be deduced from this ratio as discussed below. Let the fission yield of a selected burnup monitor (say ^{143}Nd) for the given fuel be Z. It means that, for 1 at.% fission, 1 atom out of 100 heavy atoms has undergone fission, leading to the formation of Z atoms of ^{143}Nd and thereby leaving behind (100 − 1) residual atoms of heavy elements (H).

Hence, for 1 at.% fission, the ratio (A/H) becomes

$$\frac{\text{number of atoms of } ^{143}\text{Nd}}{\text{number of atoms of H}} = \frac{Z}{(100-1)}$$

and for X at.% fission,

$$\frac{\text{number of atoms of } ^{143}\text{Nd}}{\text{number of atoms of H}} = \frac{ZX}{(100-X)}$$

Therefore, if K is defined to be

$$K = \frac{\text{number of atoms of H}}{\text{number of atoms of } ^{143}\text{Nd}}$$

then,

$$K = \frac{100-X}{ZX} = \left(\frac{100}{ZX} - \frac{1}{Z}\right)$$

From the above equation, X (in at.% fission) = $100/\{(KZ)+1\}$.

In the present study, we have used U for the heavy elements. Hence, if we experimentally know the ratio of heavy residual atoms to that of a selected burnup monitor, then the burnup can be determined, using the appropriate fractional fission yield (FFY) value reported for a fuel of known composition.

For the determination of burnup using a burnup monitor, the fractional fission yield of the burnup monitor is taken from the literature [17]. For instance a MOX fuel, such as the proposed fuel for the PFBR-500 in India, will have ^{239}Pu, ^{241}Pu and ^{238}U as the major fissionable isotopes and the fractional fission yields of ^{143}Nd for these isotopes are 4.38, 4.60 and 4.56, respectively [17]. These yield values are nearly the same and enables one to use ^{143}Nd as the burnup monitor in this case. Even though in this work only U is used as the representative heavy element, experiments can be performed to measure ion signal intensities of U and Pu bearing species and sufficient resolution can be obtained through optimization of incident laser power densities.

Obviously, the linearity of the measured intensities ratio to the actual ratio in the sample needs to be improved. In the case that the observed differences arise from matrix effects (that would be different for different compositions) then several ranges of compositions can be identified where the measured intensity ratios can be linearly related to the actual ratio and then used for appropriate ranges.

As indicated above, the accuracy of this method is determined by two factors, namely, the linearity range of the calibration plot and spread in the experimental data. As one would expect higher ^{143}Nd abundance in the irradiated fuel solution compared to simulated sample containing natural Nd, the ion signal for this species gets enhanced, thereby the error on the ratio with respect to the heavy elements will tend to be less. For this method of burnup determination, an error of about ±10% in the intensity ratio would give a corresponding estimated error of ±1 at.% burnup, for a 10 at.% burnup fission fuel solution. As indicated above, by incorporating suitable modifications in the instrumental methods (rastering of the sample, use of fast SEM, etc.), it is possible to minimize the error in the intensity ratio to ±5% or better and thereby the error in the measured burnup will be less.

One of the reasons why this ratio-approach is not being used in the conventional TIMS could be the non-uniform thermal evaporation rates of different RE and heavy elements, whereas in LMS, the laser deposits considerable amount of energy in a very short time (ns) and the temperature rise could be very high, leading to comparable amount of evaporation/ionization of all the elements present in the sample.

5. Conclusion

This paper demonstrates a potential use of our laser mass spectrometry facility to determine the atom ratio of U to selected rare earth elements chosen as possible burnup monitors. The mass spectra obtained show sufficient resolution. The error spread in the calibration plot obtained for the ratio of intensities of U/RE versus the ratio of actual number of atoms needs to be improved, possibly by providing for rastering of the sample and identifying suitable compound to be added to the solution to serve as a matrix that give linearity of intensities ratio to actual atom ratio over a broader range of atom ratios. Also the pulse-to-pulse stability of the laser pulse energy needs to be maintained. The proposed LMS method is advantageous in comparison to the conventional mass spectrometry methods in use to determine the burnup of nuclear fuel, because it does not require chemical separations (to be performed on the fuel solution) and requires only a small volume of sample solution. Therefore it will be a faster method that will handle far less total activity and is also easily adoptable for remote operation.

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