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by

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APPLICATIONS OF HIGH RESOLUTION ICP-AES IN THE NUCLEAR INDUSTRY

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ABSTRACT

Application of high resolution ICP-AES to selected problems of importance in the nuclear industry is a growing field. The advantages in sample preparation time, waste minimization and equipment cost are considerable. Two examples of these advantages are presented in this paper, burnup analysis of spent fuel and analysis of major uranium isotopes. The determination of burnup, an indicator of fuel cycle efficiency, has been accomplished by the determination of ^{139}La by high resolution inductively coupled plasma atomic emission spectroscopy (HR-ICP-AES). Solutions of digested samples of reactor fuel rods were introduced into a shielded glovebox housing an inductively coupled plasma (ICP) and the resulting atomic emission transmitted to a high resolution spectrometer by a 31 meter fiber optic bundle. Total and isotopic U determination by thermal ionization mass spectrometry (TIMS) is presented to allow for the calculation of burnup for the samples. This method of burnup determination reduces the time, material, sample handling and waste generated associated with typical burnup determinations which require separation of lanthanum from the other fission products with high specific activities. Work concerning an alternative burnup indicator, ^{236}U , is also presented for comparison. The determination of ^{235}U : ^{238}U isotope ratios in U-Zr fuel alloys is also presented to demonstrate the versatility of HR-ICP-AES.

Keywords: ICP-AES, nuclear fuels, uranium, lanthanum, fiber optic

1. INTRODUCTION

The determination of atom percent burnup data is important for the evaluation of spent fuel for conditioning as well as the prediction of fission products for waste disposal. Burnup is defined as the ratio of heavy atoms fissioned to the total initial heavy atoms in the fuel (heavy atoms > mass 225). The appropriate selection of burnup monitors is covered in detail elsewhere (1,2) but those most useful are ^{139}La , ^{99}Tc , ^{148}Nd and ^{236}U . The application of high resolution inductively coupled plasma atomic emission spectroscopy (HR-ICP-AES) to the nuclear field was first reported by Edelson and Fassel (3-5). Since then, the ICP-AES has found applications to isotope ratios (3-8) and to the isotopic composition of actinides (U and Pu) in nuclear fuel re-processing streams (4,7). Goodall and Johnson (8) extended the scope of the HR-ICP-AES to include solid sampling. They used laser ablation ICP-AES to determine uranium isotope ratios accurately and precisely directly from simulated solid metallic alloy reactor fuel samples.

The ability to determine ^{139}La in spent fuel without removal from a hot cell facility or a shielded glovebox removes the need for separation of the fission products from the samples. It must be noted here that conventional commercial ICP-AES instruments do not exhibit the sufficient optical resolution to perform this determination. Also, it should be stated that commercial inductively coupled plasma mass spectrometers (ICP-MS) do have the capability to perform the determinations, but the internal components of the instrument become excessively contaminated, severely hampering future maintenance of the instrument. The technique presented here results in a variety of benefits which include: reduced radioactive waste, reduced sample preparation effort, increased sample through-put, and limited exposure to radioactive fields. The use of a fiber optic allows the analytical signal to be transmitted from the shielded glovebox to the high resolution spectrometer. Total and isotopic uranium amounts are determined by thermal ionization mass spectrometers (TIMS) which allows for the

calculation of atom percent burnup. Experiments regarding a second burnup indicator, ^{236}U , are also presented for comparison.

One can measure total and isotopic uranium also by HR-ICP-AES. In case of the determination of total uranium content in a sample this is not a revelation, however, the accurate and precise determination of the major isotopes of uranium, ^{235}U and ^{238}U , is a newer development.

Work regarding the determination of the isotope ratios in two types of metallic alloy fuel will be presented. This type of analysis will not supplant TIMS analysis but complement it in instances where sample preparation, retrieval of samples from a remote environment or turn-around time make TIMS a less attractive option.

2. EXPERIMENTAL

A schematic representation of the experimental setup is shown in figure 1. The ICP is housed in a commercially constructed radiologically shielded glovebox. The ICP source (ARL Fisons, 3580 B, MA, USA) consists of a Fassel type minitorch and a RF generator operated at 27.12 Mhz. Solution is delivered to the micro concentric nebulizer (Cetac Technologies Ltd., Omaha NE, USA) through a laboratory constructed flow injection system with a one milliliter loop. The micro concentric nebulizer is mounted in a Scott type spray chamber. Emission from the analytical region of the plasma is transmitted by a 31 m fiber optic bundle (Fiber Guide Ind., Stirling, NJ, USA). The fiber optic bundle consists of 10-100 micron diameter fibers. The fibers at the anterior end (ICP) form a circle, while those at the posterior end form a line to match the slit of the monochromator. This results in an optimal amount of light entering the monochromator. The high resolution monochromator (THR 1500, JY Instruments SA, Metchen, NJ, USA) has a focal length of 1.5 m and is fitted with a 2400 lines/mm grating. The monochromator is operated in the double pass configuration resulting in an effective focal length of 3.0 m. The monochromator stepping motor was controlled by a Specrolink control unit (ISA Inc., Metchen, NJ, USA). The photomultiplier tube was cooled using a thermoelectric device. Current to voltage conversions were performed using a picoammeter and analog to digital conversions were made with an eight channel simultaneous analog to digital converter (DT2838, Data Translation Inc., Marlboro, MA, USA). Data acquisitions was controlled and data processed through software written in DT-VEE visual programming language (Data Translation Inc., Marlboro, MA, USA). Additional data processing was accomplished with a separate software package (PeakSolve, Galactic Ind. Corp., Salem, MA, USA). Operating conditions are presented in Table I.

Matrix matched samples were prepared by dilutions from concentrated stock solutions (U 10,000 $\mu\text{g/ml}$, Zr 1000 $\mu\text{g/ml}$, La 1000 $\mu\text{g/ml}$, SPEX Chemical, Metchen, NJ, USA). Calibration standards for lanthanum ranged from 0-1000 $\mu\text{g/ml}$ in a matrix of 180 $\mu\text{g/ml}$ of U and 20 $\mu\text{g/ml}$ of Zr.

Weighed samples were placed into a 250 ml graphite bottomed beaker. Enough nanopure water is added to cover the sample. 50 ml of premixed 16 M HNO_3 -0.5 M HF was added and the beaker covered with a Teflon cover. The sample is placed on a hot plate and was heated until the sample is dissolved. 25 ml of 1 M HNO_3 was added and the sample was heated until the volume was less than 40 ml and the precipitate (if any) dissolved. The sample was then quantitatively transferred to a pre-weighed 100 ml bottle, brought up to volume and the final mass determined. Additional dilutions were carried out in the analytical laboratory hot cells with 2 M HNO_3 .

A Finnigan MAT thermal ionization mass spectrometer (Model 262, Marietta, GA, USA) was used to determine the total and isotopic composition of the uranium in the fuel samples.

The laser system utilized for the ablation experiments was a Surelite I, Nd:YAG (Continuum Laser Corp, Santa Clara, CA). It was operated at 10Hz with a temporal pulse width of 6ns at a wavelength of 532nm. The standards used to calculate the spectrometer for the uranium isotopic work were obtained

from New Brunswick Laboratory (Argonne, IL) with the ^{236}U spike being obtained from Oak Ridge National Laboratory.

3. RESULTS AND DISCUSSION

3.1. Determination of ^{139}La by HR-ICP-AES

The ease of use and elegance of a direct optically based analysis method for the determination of atom percent burnup makes the method presented here very attractive for a typical radio-chemist. No complicated, waste-generating separation is required prior to analysis. The accuracy and precision of this technique make it useful for its stated goal: determination of atom percent burnup in irradiated nuclear fuel.

The use of ^{139}La as a monitor for the fission of ^{235}U is well established (1, 9, 10). Lanthanum is an acceptable indicator because it is formed in good yields, is monoisotopic and is stable. The thermal fission yield for ^{139}La from ^{235}U is 0.0631 (11). The decay scheme, with associated half lives in parentheses is:

An important concern in the analysis of spent fuel samples is personnel exposure from radiation fields. The radiation from a diluted dissolution of fuel is not from the ^{139}La , but from other fission products from the fuel, or the stainless steel cladding that encompasses the fuel rod. Primary contributors to the radiation fields are ^{137}Cs , ^{144}Ce , ^{90}Sr , and ^{60}Co . The method presented here results in negligible exposure to analysts due to three factors. These three factors are: 1) use of an extremely dilute solution of the spent fuel, approximately 1 g in 500 ml, 2) the use of the micro concentric nebulizer allows for a complete triplicate analysis using only 1 ml of the dilute solution, and 3) the shielded glovebox and efficient sample manipulation minimize close analyst contact.

A fiber optic high resolution spectra of the La(II) 333.75 nm line is shown in Fig. 2. The scan covers approximately forty picometers and the scan time was two minutes. The first peak shown is a minor line for the U matrix component ($180 \mu\text{g ml}^{-1}$), with the La line being at 333.749 nm. It is this U spectral line and another to the low energy side of La that interfere with conventional ICP-AES analysis. The spectra was put through a fifteen point Savitsky-Golay smoothing routine. A calibration curve generated with matrix matched La standards ranging from 0.0-1000 ng ml^{-1} , 0.0-1000 ppb, at the conditions given in Table I is shown in Fig. 3. Figures of merit for the calibration curve are a correlation coefficient of 0.9997, detection limit, ($C_L, 3\sigma$) of 20 ng ml^{-1} and a sensitivity of 6.2 E-3 arbitrary units per ng ml^{-1} . The level of quantification ($3 \times C_L$) is estimated at 60 ng ml^{-1} or 0.71 atom % burnup (for typical sample weights and dilutions).

Actual spent fuel rods from the Experimental Breeder Reactor II (EBR-II) were analyzed. Each sample analyzed is a representative portion of a fuel rod. In all, 3 fuel rods were divided into 9 samples, with the bottom (1.85-2.11 in.), middle (8.18-8.44 in.) and top (13.98-14.24 in.) of each pin being digested, diluted and analyzed separately. The nine samples were run in triplicate with a check standard after every two samples. The concentrations of La determined for each of the nine samples analyzed is presented in Table II. The precision of each sample was, in general, less than 4% for three replicates, and in most cases $\leq 2\%$ RSD. TIMS was used to determine the total U content in the fuel samples. It is essential for the calculation of atom percent burnup to know the total amount of U in each sample. Uranium is the primary heavy metal constituent present, although minute amounts of ^{239}Pu and ^{240}Pu are also present. The precision of the determined values for the total U, ^{235}U and ^{238}U is less than 0.5%

(RSD). For the sake of brevity these values are not reported here, but they were used to calculate the atom percent burnup.

3.2. Calculation of Atom Percent Burnup

The calculation of atom percent burnup from the information presented in Table II is straight forward once the original sample mass, original dissolver solution mass, total and isotopic uranium, and the precise dilution information is known. The equation is given in 1a & 1b and a sample calculation for sample #1 is presented below for clarity. The results for all samples are represented graphically in Fig. 4.

$$(1a) \text{ (mass of La created)} \times A = \text{(mass of U consumed)}$$

$$(1b) 100\% \times \frac{\text{(mass of U consumed)}}{\text{(mass of U remaining)} + \text{(mass of U consumed)}} = \text{atom \% burnup}$$

A = A constant, dependent on the molecular weight of La, fission yield for La and molecular weight of U

Sample Calculation:

$$4.46 \text{ mg La} \times \frac{1 \text{ mol}}{139 \text{ g}} \times \frac{6.02 \text{ E}23 \text{ atoms}}{1 \text{ mol}} = 1.93 \text{ E}19 \text{ atoms of La}$$

$$0.93 \text{ E}19 \text{ atoms of La} \times \frac{1}{.0631} = 3.06 \text{ E}20 \text{ atoms of U burned up}$$

$$3.06 \text{ E}20 \text{ atoms of U burned up} \times \frac{1 \text{ mol}}{6.02 \text{ E}23 \text{ atoms}} \times \frac{235 \text{ g U}}{1 \text{ mol U}} = 0.119 \text{ g of U burned up}$$

$$\frac{0.119}{[0.119 \text{ g of U B.U.} + 1.384 \text{ Total g of U}]} \times 100\% = 7.91\%$$

The above sample calculation does not take into consideration the minor effects of the other fissile elements or isotopes that may contribute, to a small extent, to the production of lanthanum in a reactor setting. The value of 1.384g of U remaining was provided by mass spectrometry which is performed routinely on each fuel dissolver solution to obtain fissile content.

The contour of the plot for each fuel rod is characteristic of the reactor and fuel type being analyzed (9, 10). this trend shows the highest burnup in the center of the rod, with the bottom being second highest and the top having the least amount of fissions. The burnup trend is a result of the characteristic neutron flux of the reactor and the relative positions of the fuel rods in the core. The results presented here are consistent with results presented previously (9, 10) for this reactor and arrangement of the fuel rods.

3.3. Isotopic analysis by HR-ICP-AES

The standard technique for determining isotopic compositions of actinide elements is TIMS. This technique is accurate and very precise but frequently requires tedious sample preparation and analyte separation. If you do not require the extreme precision and accuracy of TIMS, then alternative methodologies based upon atomic spectrometry, such as ICP-MS or ICP-AES, may be advantageous. The use of ICP-MS for isotopic analysis is obvious, but the use of ICP-AES is more obscure and relies upon isotopic splitting of emission lines. Relatively large splitting is observed for the actinides and these may be used to extract isotopic information using spectrometers of moderate- to high-resolving power (12). For example, the U(II) 424.37-nm emission line is split isotopically, the separation of the ^{235}U and ^{238}U components being $\approx 25 \text{ pm}$. Kuhn deals with the theory of isotopic splitting (13), and compendia of isotope shifts (14,15) are available.

High-resolution ICP-AES was applied to the determination of ^{235}U : ^{238}U isotope ratios in metallic fuels. Conventional pneumatic nebulization and laser ablation were used for sample introduction to the ICP. Two different alloys (Mk. III and Mk. IV) of identical nominal chemical composition (90% m/m U, 10% m/m Zr) but different levels of ^{235}U enrichment, (for example, Mk. III = 66.9% ^{235}U , Mk. IC = 69.5% ^{235}U) were analyzed. Reference values for the $^{235}\text{U}/^{238}\text{U}$ isotopic ratios, as determined by TIMS, were $2.094 \pm 0.025\%$ (Mk. III) and $2.381 \pm 0.025\%$ (Mk. IV). The alloys were brought into solution by digestion with nitric:hydrofluoric acids. The laser ablation was performed using 532-nm radiation with a pulse energy of 125 mJ.

Figure 5 shows examples of the emission spectra of the U(II) 424.4-nm line for both Mk. III and Mk. IV alloys. After background subtraction, we ratioed the peak ^{235}U emission with respect to the peak ^{238}U emission yielding values of 2.04 (Mk. III) and 2.28 (Mk. IV). These results suggested a small negative bias of $\approx 3\text{-}5\%$ in the determination. This bias may be caused by a slight difference in the line width of the two emission features, which in turn, could be caused by the hyperfine splitting present in the ^{235}U , but not in the ^{238}U line. The application of an empirical correction factor derived from the measurement of the solution emission ratios of certified reference materials provided a means of correcting for this apparent inaccuracy. The emission ratios of the isotopically shifted line pair of the U(II) 424.37-nm emission line were determined for six certified reference materials of known isotopic composition (NBL 100-930). This was repeated for a total of five sets of measurements, each on a separate day. The equation for the resultant isotope ratio was:

$$^{235}\text{U}/^{238}\text{U} \text{ Isotopic Ratio} = [(^{235}\text{U}/^{238}\text{U} \text{ Emission Ratio}) + 0.0127] / 0.9820$$

This expression was applied to all subsequent determinations of U isotopic ratios.

The application of internal standardization improved the precision of the determination of the isotopic ratio for both conventional concentric nebulization and LA-ICP-AES. Table III shows the efficacy of this correction for determinations using both conventional concentric nebulization and LA-ICP-AES. In all cases the precision improvement was highly significant (99% confidence). Internal standardization corrects for the temporal separation of the measurement of the two components of the U emission line, which was inherent when using a scanning monochromator. Internal standardization was applied to all subsequent determinations of ^{235}U : ^{238}U isotopic ratios. Zr was added as an internal standard to normalize out any instrumental functions that may occur and also it is present in the samples in any case.

Table IV shows the accuracy and precision to the determination of ^{235}U : ^{238}U isotope ratios by conventional and LA-ICP-AES. These isotopic ratios are statistically indistinguishable from the TIMS values at the 99% confidence level. This clearly demonstrates the potential to determine the isotopic composition of the actinides and that LA-ICP-AES is capable of producing accurate and precise results. The precision is typically an order of magnitude worse than data obtained with TIMS. The precision of the LA-ICP-AES method is poorer than that obtained with conventional concentric nebulization. However, the rapidity of the ICP method using laser ablation and an analysis time of ≈ 2 min allows rapid screening of materials with minimal sample preparation and consumes < 1 mg of sample per determination. This is highly attractive for the analysis of irradiated and transuranic-containing material such as spent fuels and wastes.

Figure 6 presents another application of HR ICP-AES. This is the spectrum of a synthetic spent fuel dissolver solution. The atom % burnup is 12.5 % which is equivalent to 2.5 atom % ^{236}U . The ^{236}U is created via neutron capture by ^{235}U . The detection limit for this method is 3.0 atom % burnup versus 0.5 atom % burnup for the ^{139}La method.

4. SUMMARY

This paper presents a time-saving, elegant and precise method for determining atom percent burnup for irradiated nuclear reactor fuel. A fuel segment is dissolved in acid and a dilute solution of this is used to optically determine the ^{139}La content. ^{139}La is a stable isotope produced from the fissioning of the heavy atoms, specifically ^{235}U present in the fuel. The technique provides for precise (<4% RSD) ^{139}La determinations with no spectral interference from other species present. This method can be safely implemented using a conventional ICP enclosed in a shielded glovebox. The analytical figures of merit presented indicate that this technique is applicable for samples of a like matrix that exhibit an atom percent burnup of $\geq 1\%$. An alternative burnup indicator was also examined and determined to be feasible but inferior to ^{139}La .

The versatility of HR-ICP-AES was demonstrated by applications to the determinations of the $^{235}\text{U}/^{238}\text{U}$ isotope ratio of metallic alloy fuel yielding information that was both precise and accurate. This type of analysis may have applications in either fuel fabrication or waste treatment fields where fields where rapid, remote method is attractive.

An improvement that has been implemented and is awaiting final testing is to utilize a larger diameter single fiber instead of a bundle. The advantage is that the fiber can be more easily split into two pieces at the glovebox interface thus keeping the majority of the fiber clean of contamination. Also this allows for the replacement of the optical "pigtail" with one of variable lengths which may be useful for other experiments. In addition our experience has shown that the probability of breakage increases with the difficulty in performing the repair, i.e., the portion in the glovebox nearly always breaks first.

5. ACKNOWLEDGMENTS

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Table I. Operating conditions for FO-HRC-ICP-AES used in the determination of atom percent burnup

Forward power	680 W
Reflected power	<5W
Nebulizer type	Micro concentric
Nebulizer flow	0.080 ml min ⁻¹
Viewing height	≈9 mm
Gas flows	
Coolant	7L min ⁻¹
Auxilliary	0.5 L min ⁻¹
Nebulizer	35 psi Ar
Emission Line	333.749 nm
Monochromator scan speed	20 pm min ⁻¹
ADC sampling rate	1000 Hz

Table II. Amount of ¹³⁹La for the nine fuel samples analyzed

Sample	¹³⁹ La(mg)	%RSD
1	4.46	2.9
2	4.24	0.8
3	3.06	2.5
4	4.21	1.7
5	4.00	0.04
6	3.03	2.0
7	3.39	2.1
8	3.68	3.5
9	2.95	0.9

Table III. U Isotope ratio determinations. Improvement in application of an internal standard.

Internal Standard?	Sample-introduction method	% Relative standard deviation
No	Conventional concentric nebulization	1.64 (n = 5)
Yes	Conventional concentric nebulization	0.17 (n = 5)
No	Laser ablation	7.02 (n = 27)
Yes	Laser ablation	1.27 (n = 27)

Table IV. Determination of U isotopic ratios (²³⁵U/²³⁸U) by LA-ICP-AES

Alloy	Laser-ablation ICP-AES	Conventional nebulization ICP-AES	TIMS
Mk. III	2.092 ± 1.27%	2.091 ± 0.29%	2.094 ± 0.025%
Mk. IV	NA	2.40 ± 0.59%	2.381 ± 0.025%

Figure 1. Experimental setup for HR-ICP-AES. Major components include the ICP glovebox, fiber optic, high resolution monochromator and computer controlled data acquisition system.

Figure 2. HR-ICP-AES scan of the ^{139}La line (333.749 nm) obtained at the operating conditions given in Table I. La concentration is $1 \mu\text{g ml}^{-1}$ and the matrix consists of $180 \mu\text{g ml}^{-1}$ U and $20 \mu\text{g ml}^{-1}$ Zr.

Figure 3. Analytical calibration curve for ^{139}La generated at the experimental conditions given in Table I. Error bars are omitted, as they are contained within the symbol for each data point.

Figure 4. Plot of atom % burnup vs. rod section for the 9 samples (3 fuel rods) determined at the operating conditions given in Table I. Samples exhibit the expected trend for bottom, middle and top sections of the rod. Error bars are omitted as they are contained within the symbol for each data point.

Figure 5. HR-ICP-AES spectrum of Mk. III and Mk. IV fuels (424.437 nm emission line for ^{238}U).

Figure 6. HR-ICP-AES spectrum of synthetic fuel solution. Total uranium concentration is $600 \mu\text{g}/\text{cm}^3$ spiked with pure ^{236}U ($12 \mu\text{g}/\text{cm}^3$ or 2.5 atom percent) and zirconium concentration is $100 \mu\text{g}/\text{cm}^3$. Wavelength is 424.437 nm. Wavelength difference between ^{235}U and ^{238}U lines is 25 pm. Experimental and fit data are overlaid.