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HIGH RESOLUTION EMISSION SPECTROSCOPY IN A
LASER INDUCED PLASMA

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Pu-239/Pu-240 isotope ratios determined using high resolution emission spectroscopy in a laser induced plasma

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Abstract

Isotope ratios for plutonium can be determined through direct observation of atomic emission spectra at high resolution. The plutonium atomic line at 594.52202 nm has been previously cataloged with a Pu-240/Pu-239 isotope shift of -0.355 wavenumbers using a microwave electrodeless discharge tube and a 9-m photographic plate emission spectrograph [1]. This isotope shift has now been clearly resolved from a laser induced plasma. Atomic emission was dispersed through a 2-m spectrometer in double pass mode and collected on an electronically gated, intensified charge-coupled device (ICCD) camera. Curve-fitting software was used to produce integrated peak areas whose ratios closely match known isotope ratios. Observed plutonium linewidths were on the order of 0.0066 nm. The instrument-limited linewidth was calculated to be 0.0052 nm, based upon the known modulation transfer function for the ICCD system.

Keywords: laser-induced plasma, Pu, isotope ratio, emission spectroscopy

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) has received considerable attention as a versatile analytical tool, particularly in the past decade, with many reviews being written [2-4]. The technique has several advantages over other forms of analysis. The Los Alamos Plutonium Facility currently employs standard ICP-MS/AES for most chemical analyses, with dissolution of a fairly large sample (~0.5 g) normally required. Isotope ratios are determined by thermal ionization MS. Analyses for either actinide isotopic ratios or impurity elements normally requires that the actinide components (chiefly U, Pu, and Am) be first separated from the matrix using anion exchange chromatography in order to avoid interferences. This step adds to quantitative uncertainty, especially with respect to impurity analyses. The advantages of LIBS for nuclear applications are well known [5], and those of greatest importance at the Plutonium Facility include reduction of sample size, direct analysis in inhomogeneous matrices, reduced turnaround time between sample submittal and results, and *in-situ* analysis capability. LIBS has been previously applied to actinide analysis [6-10], including recent work involving U isotope ratio analysis [11].

Observation of isotope shifts via optical emission spectroscopy is not a common application for LIBS, mainly due to the very high resolution needed. However, reference [11] does report a LIBS isotope ratio determination for U-238/235, conducted in-line as part of an isotope separation process. Analysis was performed on a U(II) emission line, with linewidths approximately twice as broad as the instrument limit. We report observation of the plutonium 240/239 isotope shift from Pu(I) emission with linewidths

approaching our instrument limit. We will show that the results for uranium presented in reference [11] compare favorably with the plutonium results presented here, and underscore the viability and usefulness of high-resolution LIBS for *in-situ* isotopic analysis work.

2. Experimental

The LIBS system employs the following major components: a pulsed laser, sample chamber, emission spectrometer, detector, and computer. Work within the Plutonium Facility requires that radioactive samples be contained inside a glovebox. Only the sample chamber and a minimum of optics reside within the glovebox; all other optical components are mounted on external optical tables. Refer to Figure 1 for a diagram of the experimental layout. The laser used was a Continuum Surelite I[®], a pulsed and Q-switched Nd:YAG operating at its fundamental wavelength of 1064 nm. This laser generates pulsewidths of ~5 ns and is capable of more than 400 mJ/pulse. However, the energy is typically attenuated to ~25 mJ. Conventional optics are used to direct the beam through a viewport in the side of the glovebox, ultimately to be focused into a <100 μm spot on the sample surface, producing an energy density of $\sim 10^{11}$ W/cm². The sample chamber consists of a custom-made vacuum chamber utilizing conventional Conflat[®]-type ultra-high vacuum flanges for viewport mounting. A remotely operated 3-axis translation stage mounted within the chamber allows for sample manipulation. Data was typically collected in an atmosphere of 100 torr helium. Emission was collected using conventional optics, with light exiting the glovebox through a second viewport and focused onto the entrance slit of a spectrometer. The spectrometer used was a McPherson model 2062DP, a 2-meter Czerny-Turner type with double-pass mode. The unit currently employs a 120x140 mm holographic grating with 2400 gr/mm. The reciprocal linear dispersion is 0.19 nm/mm in single-pass mode. The entrance slits were adjusted to maximize signal without sacrificing linewidth. We found that linewidths began to increase for entrance slit widths in the range of ~35-50 μm . A slit width of 35 μm was usually sufficient to avoid broadening, and typically used for data collection. A Princeton Instruments model ICCD-576E-R/B intensified CCD camera was used in lieu of an exit slit. This detector uses an 8x15 mm CCD array with 384x576 pixels; pixel size is 22x22 μm . Although the pixel width along the horizontal (wavelength) axis is 22 μm , the instrument-limited linewidth is governed by the overall detector resolution. The resolution for the intensifier is defined by the manufacturer's specification of 55 lp/mm at 5% of the modulation transfer function (MTF). The ICCD was delayed and gated by a Princeton Instruments model PG-200 pulse generator, with a working delay range of 28 ns – 80 ms and fully adjustable gate. Data was typically collected with a delay of 1 μs and a gate of 5 μs . Data was collected using Princeton Instruments software WinView[®] v.2.2.1, which facilitates interface between the Princeton Instruments model ST-138S ICCD controller and a Micron 266 MHz PC running Windows NT v.4.0. Data was manipulated in WinView[®] and then converted to ASCII-XY for analysis by curve-fitting program PeakFit[®] v.4.0 (SPSS, Inc.).

3. Results

Reference [1] contains an impressive compilation of plutonium emission lines at very high resolution (8 significant figures). More than 30,000 lines are cataloged, and a great many are accompanied by observed Pu-240/Pu-239 isotope shifts (IS). A transition was selected that possessed both a large IS and high intensity, with minimal spectral interference from neighboring lines. Short delay times (~ 100 ns) are dominated by ionic emission and a broad continuum due to bremsstrahlung radiation from electron-ion collisions [4]. Emission observed at longer delay times are usually dominated by atomic emission as the plasma cools and more electron-ion recombinations occur. As a result, long delay times generally favor atomic emission as well as narrow linewidths due to a decrease in Stark broadening. Thus the Pu atomic line at 594.52202 nm (16815.576 cm^{-1}) was chosen for analysis, with a previously observed Pu-240/239 $\Delta IS = -0.355\text{E-3 cm}^{-1}$ [1]. A relatively long ICCD delay of 1 μs was used. These conditions afford both good intensity and linewidths sufficiently narrow to resolve the Pu isotope shift.

Two samples of greatly differing isotopic composition were chosen for characterization. The first sample consisted of Pu metal of a nominal 239/240 isotopic ratio of 93/6. The second sample was PuO_2 of nominal composition 49/51. The oxide sample was analyzed as a pressed pellet. Data was initially collected as a wavelength-dispersed 3-dimensional image spectrum. Each 3D spectrum was then reduced to a 2D intensity vs pixel plot for curve fitting. The intensity axis of a 2D plot represents a sum, or "bin" of the vertical position channels appearing in the image spectrum. Figures 1 and 2 depict the 93/6 and 49/51 ratio samples as 2D spectra, with some vertical channels binned. The number of vertical channels chosen for binning depended on the relative signal-to-noise of the data. Observed linewidths were relatively insensitive to the vertical position of the plasma image at the 1 μs delay time. Additionally, precise alignment of the vertical axis of the ICCD camera with the entrance slit axis was difficult, and could vary ± 0.5 pixel from the top of the CCD to the bottom. This effect can artificially broaden the linewidth if all 384 vertical channels were binned. Therefore, each image was critically analyzed and the number and position of binned channels were chosen to minimize linewidth and maximize intensity. The data was imported into PeakFit[®] as ASCII-XY. A simple linear 2-point baseline fit and subtraction was implemented. The data was then sectioned to include ~ 25 -30 pixels, centered on the Pu(I) peak at 594.52202 nm. A Gaussian-Lorentzian sum algorithm was chosen, with fitted linewidths shared between the peaks. Sharing of linewidths assumes that both isotope peaks exhibit equal Doppler (Gaussian) and Stark (Lorentzian) broadening. The fitting program typically converged in about 7 iterations, with $r^2 \sim 0.99$. Refer to Table 1 for a summary of results for the two samples.

4. Discussion

The curve fit typically produces a peak separation of ~ 7.2 pixels, with full-width at half-maximum (FWHM) ~ 3.2 pixels. Expected dispersion for the 2-m spectrometer in double-pass mode (2400 gr/mm grating) is 0.095 nm/mm. The ICCD uses $22 \times 22\text{ }\mu\text{m}$ pixels, which translates to 2.09E-3 nm/pixel . The

Pu-240/239 isotope shift is known to be -0.355 cm^{-1} , or $1.255\text{E-}2 \text{ nm}$ [1], with Pu-239 occurring at 594.52202 nm and Pu-240 at 594.53457 nm. This wavelength difference spans 7.2 pixels and we obtain $1.74\text{E-}3 \text{ nm/pixel}$. If we assume $1/(0.022) = 45.45 \text{ pixels/mm}$, we obtain 0.079 nm/mm . Although a crude measurement, this dispersion compares reasonably well with the known dispersion of the spectrometer. It can be seen that this isotope shift is resolved at nearly the limit of the spectrometer, with only 3.2 pixels used to define the lineshape. Most spectroscopic applications require a minimum of 5 data points (or pixels in this case) to adequately define a lineshape. Therefore, the following discussion involving lineshapes and line positions may be regarded as semi-quantitative, and no error limits will be reported. We generally regard the precision of data acquisition and curve-fitting as ± 0.5 pixels in relation to both line positions and linewidths presented in this work.

Resolution of the ICCD system is dependent on three major components: intensifier tube, fiber optic coupler, and CCD. As described in the Experimental section, the intensifier tube used with this particular ICCD system has a fixed resolution as described by its intrinsic MTF. The fiber optic coupler possesses a very fine pitch that is much smaller than the CCD pixel size ($\sim 6 \mu\text{m}$ versus $22 \mu\text{m}$) and will be assumed to have a negligible effect on system resolution. The CCD pixel size also plays an important role in overall system resolution, and the CCD MTF must be combined with the intensifier MTF in order to calculate a system resolution. Since determination of system resolution (and thus the instrument-limited linewidth) is essential for this discussion, we will develop these ideas further. The goal of the following discussion is to show that under the LIBS conditions presented in this paper, the plutonium linewidth observed is nearly instrument-limited, and that little contribution from intrinsic Doppler or Stark broadening is observed.

4.1 Intensifier Tube Resolution

Like the overall ICCD system, the intensifier tube is comprised of the following major components, whose effects combine to determine its overall resolution: a photocathode, microchannel plate, and phosphor screen. Intensifier manufacturers typically report resolution in terms of a MTF, which may be defined as the contrast response of the intensifier tube system at a specified resolution. The resolution is expressed as a spatial frequency, f , in units of line pairs per millimeter (lp/mm). Ideally, the modulation of an intensifier decreases exponentially with resolution [12]:

$$(1) \text{ MTF}_i(f) = \exp(-c*f), \text{ where } c \text{ is a constant}$$

The MTF function may be obtained by an exponential fit of instrument response at many spatial frequencies. Alternatively, the MTF may be measured through the Fourier Transform of the line spread function (LSF). The LSF is defined as the system response to a point (or impulse) input. In lieu of the LSF, the intensifier manufacturer generally reports the spatial frequency at 5% modulation and exponential functionality is

assumed. In the present case, the intensifier specification provided (55 lp/mm at 5% MTF) allows calculation of an exponential coefficient, $c=0.5447$.

4.2 Intensifier/CCD System Resolution

The ideal CCD response exhibits $\text{sinc}(fx)$ functionality [12-14]:

$$(2) \text{MTF}_{\text{ccd}}(f) = \sin(2\pi fx/2)/(2\pi fx/2), \text{ where } x \text{ is the pixel size in mm.}$$

The combined system MTF is obtained by multiplication of the intensifier MTF with that of the CCD [12]:

$$(3) \text{MTF}_{\text{sys}}(f) = \text{MTF}_i(f) * \text{MTF}_e(f) = \exp(-c*f) * \sin(2\pi fx/2)/(2\pi fx/2)$$

Since both the intensifier MTF and the CCD pixel size are known, the system MTF may be calculated. The MTF curves for the intensifier, CCD, and system are depicted in Figure 3.

4.3 Determination of Instrument-Limited Linewidth

As mentioned in the Experimental section, LIBS spectra were fitted using the program PeakFit[®] and a Gaussian-Lorentzian Sum (area) algorithm. This function has the following form:

$$(4) \quad y := 2 \cdot a_0 \cdot \left[\frac{a_3}{a_2} \cdot \frac{\sqrt{\ln(2)}}{\sqrt{\pi}} \cdot e^{\left[-4 \cdot \ln(2) \cdot \left(\frac{x-a_1}{a_2} \right)^2 \right]} + \frac{(1-a_3)}{\pi a_2 \cdot \left[1 + 4 \cdot \left(\frac{(x-a_1)}{a_2} \right)^2 \right]} \right]$$

where a_0 = area
 a_1 = center
 a_2 = width
 a_3 = shape

The fit for the Pu-239 line at 594.522 nm (93/6 isotopic ratio sample) yields the following parameters:

$$\begin{aligned} a_0 &= 1.67\text{E}7 \\ a_1 &= 305.2 \\ a_2 &= 3.18 \end{aligned}$$

$$a_3 = 0.186$$

Since our analysis was performed with the x spectral axis in units of pixels, the center, width and shape have units of pixel, and the area is in units of square pixel. The observed lineshape has FWHM of 3.18 pixels, or 70.0 μm .

Since the intrinsic LSF for the ICCD was not available, an empirical relationship was provided by the ICCD manufacturer [12] which relates FWHM, or spot size to system resolution:

$$(5) \text{ resolution at 50\% MTF (lp/mm)} = 0.6/\text{spot size (mm)}$$

We calculate $\text{MTF}_{\text{sys}} = 10.94 \text{ lp/mm}$, and spot size = 55 μm , or 2.5 pixels. If the functionality shown in equation (4) is assumed to apply to the intrinsic LSF for the ICCD system, and an iterative process may be used to approximate the linewidth of a point source. The width and shape terms were varied such that, when the magnitude of the Fourier transform of equation (4) is taken, the resultant MTF curve closely approximates the calculated MTF of the system. The a_0 and a_1 terms have no effect on the Fourier transform. Therefore, the best-fit parameters are:

$$a_2 = 2.7$$

$$a_3 = 0.30$$

An overlay of the two MTF curves is shown in Figure 4. The approximated point source linewidth is ~ 2.7 pixels, or $\sim 59 \mu\text{m}$. The agreement between these two methods is reasonable through the range of modulations generally encountered in spectroscopic applications, and allows a check of the empirical relationship given in equation (5). However, since the agreement of functionality is not exact, we will calculate the instrument-limited linewidth from manufacturer specifications:

$$(6) \text{ spot size (0.055 mm)} * \text{dispersion (.094 nm/mm)} = \text{instrument-limited linewidth (.0052 nm)}$$

This value is quite close to the 0.0055 nm quoted from reference [11] for a nearly identical ICCD/spectrometer system. The difference between our instrument limit and observed linewidth is approximately 0.7 pixels, or $\sim 0.14 \mu\text{m}$. This small amount of line broadening may be attributed to conditions within the plasma or to experimental error. Instrument-induced line broadening effects might be the result of slight misalignments in the optical system or the result of insufficient pixel density, resulting in an ill-defined peak and producing a curve-fitting artifact.

The uranium work referenced in [11] indicates that under other experimental conditions, a uranium plasma is dominated by ionic lines which exhibit a larger degree of broadening. Reference [11] reports observation of the U-238/U-235 isotope shift, using an ionic line at 424.437 nm with $\Delta\lambda/\lambda = 0.025$

nm, or 2.333 cm^{-1} . The line broadening observed exceeded the instrument limit by a factor of 2 (observed linewidth $\sim 0.012\text{ nm}$, instrument limit 0.0055 nm). A Doppler width of 0.0106 nm was calculated for the U(II) line, with Stark width $\sim 0.002\text{ nm}$ at a delay time of 350 ns . Although the experimental conditions of this work closely resemble the work presented here, major differences include shorter laser wavelength (308 nm excimer vs. 1064 nm Nd:YAG), lower energy density (0.46 GW vs. $\sim 10\text{ GW}$), shorter delay times ($0\text{--}500\text{ ns}$ vs. $1\text{ }\mu\text{s}$), and changes in buffer gas pressure and composition (2.67 Pa ($\sim 20\text{ mtorr}$) air vs. 100 torr He). These comparisons indicate that the plasma environment greatly affects the analyte intrinsic linewidth and thus the ability to adequately resolve isotopes when using LIBS in this application. Other plasma sources can produce quite narrow intrinsic linewidths. Recent work [15] using aqueous uranium and an ICP/AES instrument have shown that the intrinsic linewidth of U(II) at 424.437 nm is 0.0030 nm under these conditions. This is likely due to a combination of much lower U ion velocity (less Doppler broadening) and a cooler plasma temperature (less Stark broadening).

5. Conclusions

We have shown that LIBS may be applied to plutonium isotopic analysis. The technique is sensitive, essentially non-destructive, and can produce accurate results with reasonable precision. The accuracy of the technique critically depends on adequate spectral resolution of isotopic emission. The instrument-limited linewidth produced by an ICCD is dependent on the MTF of both the intensifier and the CCD, and must be accurately known before the intrinsic linewidth of an analyte is measured. The observed linewidth for Pu(I) is slightly larger than the calculated instrument limit, and broadening is estimated to be 0.14 pm . Although possibly due to plasma conditions, this degree of line broadening may be largely due to experimental error. These errors may arise primarily from (1) misalignment of the vertical axis of the ICCD with the axis of the entrance slit of the spectrometer, (2) misalignment of the ICCD with the focal plane of the spectrometer, and (3) lack of precision due to few number of data points defining the lineshape.

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Table 1 Pu 239-240 isotope ratio results

Sample	Observed Ratio	Known Ratio
Metal "H"	93.1/6.9	93/6
Oxide "AFR360"	49.0/51.0	49.6/51.4

Analysis line*	240 Isotope Shift*	Intensity*	Atomic (1) or Ionic (2)*
594.52202/16815.576 (nm/ cm ⁻¹)	- 0.355 (cm ⁻¹)	8	1

* Pu line position is for Pu-239 and quoted from reference [1]. Relative intensities are in half-log units ranging from 0-9.

Fig. 1. LIBS spectrum of plutonium metal sample with isotope ratio 93/6. The plasma image data was an integration of 900 laser shots (20 Hz for 45 sec.). Approximately 200 (out of 384) vertical channels were binned to produce a 2D spectrum containing 576 horizontal channels. The Pu-239 atomic emission at 594.52202 nm appears at pixel 305, with Pu-240 at pixel 312.

Fig.2. LIBS spectrum of plutonium oxide sample with isotope ratio 49/51. Approximately 200 vertical channels were binned. Pu-239 appears at pixel 299, with Pu-240 at pixel 306.

Fig.3. Calculated modulation transfer functions of the intensifier, CCD, and ICCD system. The curves are labeled MTF_i for the ideal intensifier response, MTF_{ccd} for the CCD, and MTF_{sys} for the ICCD system. The three MTF curves correspond to equations 1-3 (see text).

Fig.4. Comparison of calculated ICCD system MTF (MTF_{sys}) and the magnitude of the FT taken from a best-fit line spread function (MTF_{fit}). The LSF used was assumed to be influenced by Gaussian and Lorentzian factors, with the same functionality as used to fit the experimental data (equation 4, see text).