

DIRECT ISOTOPE RATIO MEASUREMENT OF URANIUM METAL BY EMISSION SPECTROMETRY ON A LASER-PRODUCED PLASMA

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The method of Optical Emission Spectrometry on a Laser-Produced Plasma (OES/LPP) at reduced pressure has been studied for the determination of the uranium isotope ratio ($^{235}\text{U}/^{238}\text{U}$). Spectral profiles of the investigated transition U-II 424.437 nm show the possibility to obtain an isotopic spectral resolution in a laser-produced plasma under exactly defined experimental conditions. Spectroscopic data and results are presented.

Keywords: Laser Ablation, Emission Spectrometry, Uranium, Isotope Control

1. INTRODUCTION

For the aim of direct elemental analytical control, laser-produced plasmas as photon source for emission spectrometry are studied by several groups [1,2]. First, all types of samples to be analyzed (metals (solid or molten), ceramics, glass, compounds, ...) can be used and this without chemical preparation. Either a global mass analysis or a localized control with the possibility of cartography can be carried out. Finally one can apply a remote analysis (hostile environment) and on-line for the control in manufacturing processes. Concerning the sensitivity of OES/LPP, detection limits of PPM's (expressed in $\mu\text{g/g}$) are found [3]; the reproducibility can be as low as some percents. For analytical purposes laser plasmas can be created at atmospheric or reduced pressure. In the case of atmospheric pressure, it is possible to obtain very good analytical results [4], but the observed emission lines are in general very broad (0.1 nm). On the other hand, it is necessary to work at reduced pressure for applications which need atomic emission with narrowest linewidths.

In this work, we study the possibility of using OES/LPP at reduced pressure (figure 1) for the determination of the uranium isotope ratio. Depending on the isotope shift of the investigated transition, we have to get a spectral resolution in the range of 0.001 - 0.01 nm to measure the isotope ratio in a direct way. Attention has to be paid at spectral interferences in the case of a complex sample matrix. Experimental conditions providing high spatial and spectral resolution during the spatio-temporal plasma expansion must be analyzed.

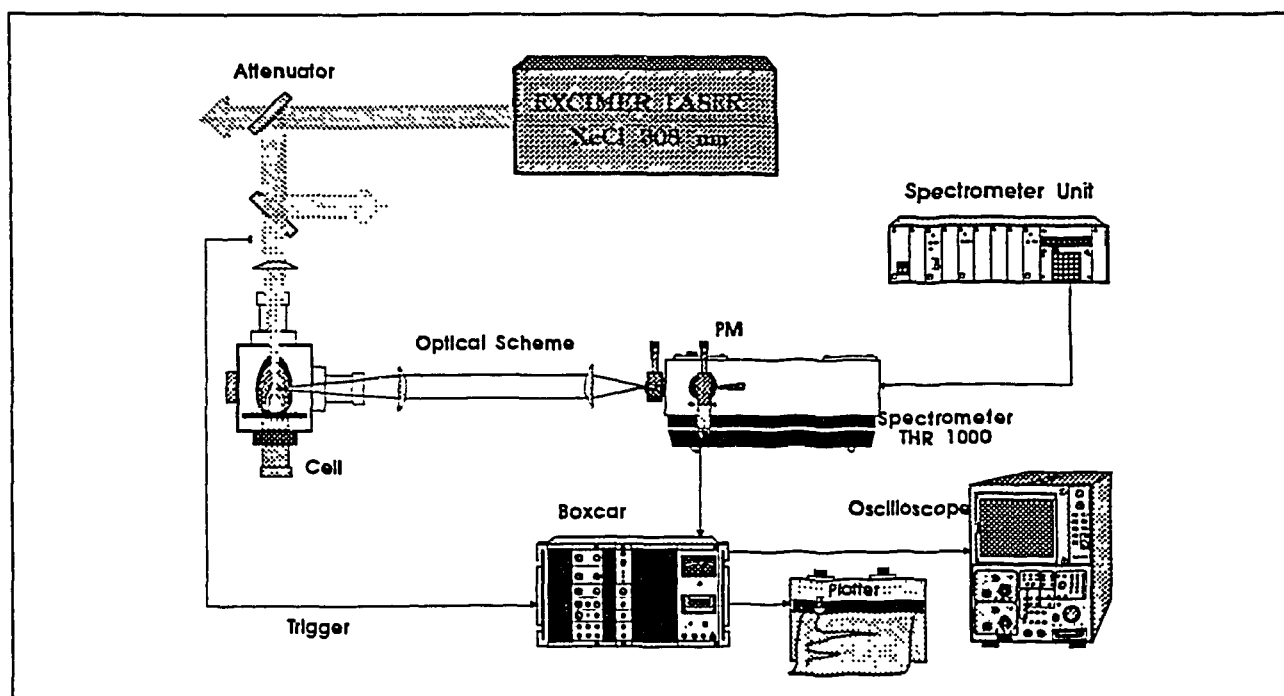


Fig.1: Experimental set-up used for optical emission spectrometry on a laser-produced plasma at reduced pressure (OES/LPP)

2. CHARACTERIZATION OF COPPER PLASMA

First experiments are performed in order to study spectral lines in a pure copper matrix. We investigate different relevant plasma parameters responsible for the measured linewidths (e.g. laser energy, time behavior of energy level population, expansion velocities of the particles above the target surface, the spatial distribution of these parameters, etc.). A best value of 0.01 nm for the linewidth (FWHM) of the Cu-I 510.558 nm transition (figure 2) is obtained at 0.6 mm height above the sample for a delay of ~ 300 ns [5,6]. Measurements are carried out with a fluence of 5.4 J cm^{-2} and at a pressure of 2×10^{-2} Torr (air).

With the help of a plasma cartography (three dimensional: x ($\equiv y$), z and t), the results obtained by optical emission spectroscopy (linewidths and intensities) are related to the spatial position of the plasma fraction investigated in the plasma plume at a certain time delay t . This plasma expansion model (figure 3) is developed by pictures taken with an intensified and gated CCD camera during the first microsecond of the plasma evolution. A gate width of 3 ns is short enough for stop-action pictures. The established relation between the full linewidth and the investigated plasma fraction can help to interpret the contribution of different plasma parameters.

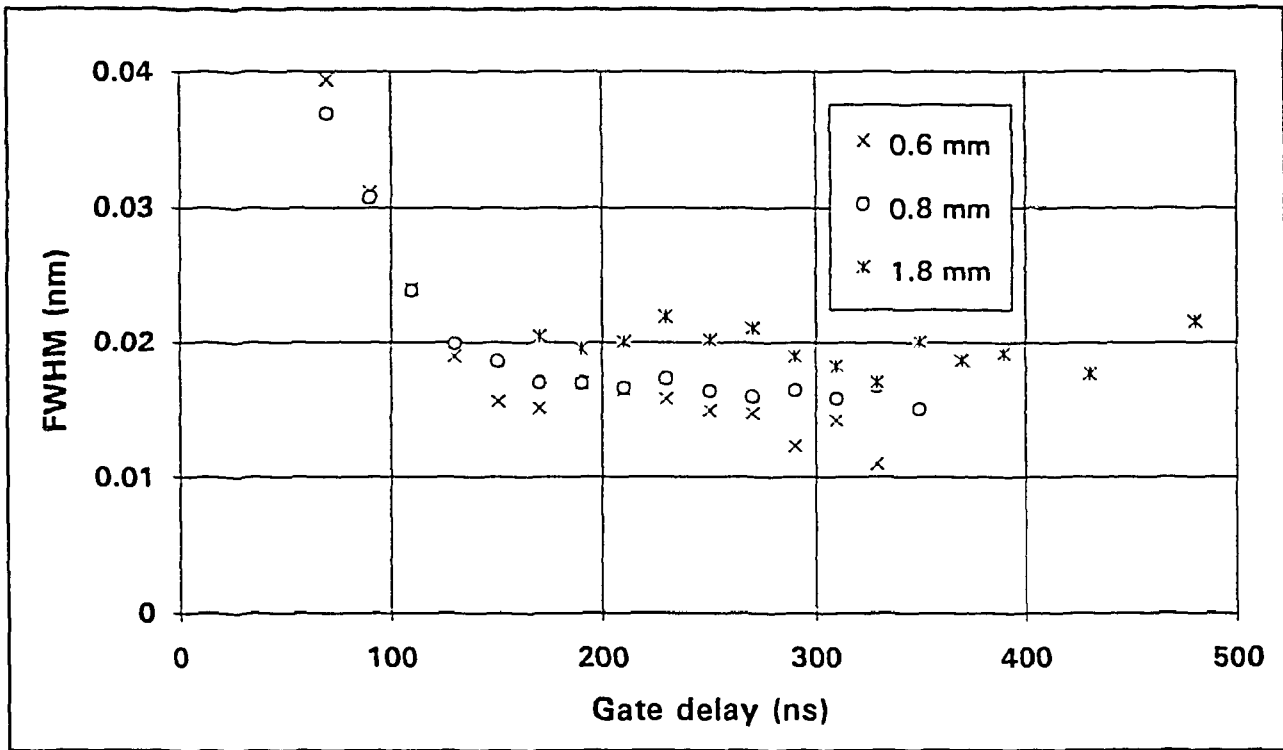


Fig.2: Linewidth distribution (FWHM) of Cu-I 510.558 nm line as function of observation height and gate delay

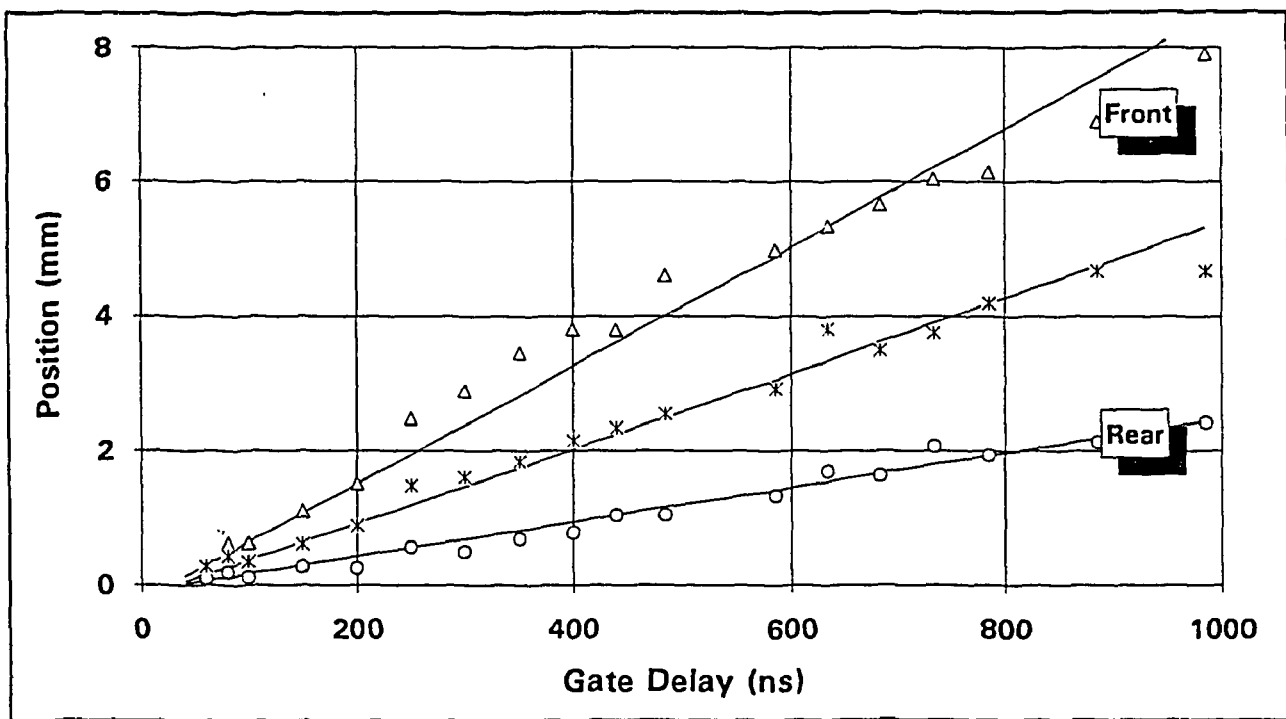


Fig.3: Expansion of the plasma front, the intensity maximum and the rear in Z as function of delay

It has been shown that Stark broadening is predominant during the first 200 ns, whereas the spectral resolution is Doppler limited for longer delays. A compilation of full linewidths to an electron density n_e gives a value of $7.3 \times 10^{16} \text{ cm}^{-3}$ for a delay of 70 ns and a height of 0.8 mm. Within the first 50 ns, the plasma is very hot and re-absorbing. This result also agrees very well with the temperature obtained by a Boltzmann plot. For delay times $t < 30$ ns we can assume an electron density of at least $3 \times 10^{17} \text{ cm}^{-3}$. Nevertheless our copper plasma is not very dense with a quite moderate value in comparison with other authors.

3. STUDIES ON URANIUM

The linewidth of 0.01 nm obtained on copper shows the interest to apply this method on elements having transitions with isotope shifts greater than 0.02 nm. Optimized experimental conditions are applied to uranium targets and the U-II 424.437 nm transition with an isotope shift of $\Delta IS = 0.025 \text{ nm}$ [7] is investigated [8]. Spatially and temporally resolved diagnostics indicate gas dynamic effects playing a dominant role in the formation and propagation of ejected material pulse. A plasma excitation temperature of $5.5 \times 10^4 \text{ K}$ and expansion velocities in the range of $9 \times 10^3 \text{ ms}^{-1}$ are revealed by TOF distribution measurements. The high expansion velocity is attributed to the fact that ions (i.e. the investigated uranium transition) are increasingly subjected to long-range plasma potentials at higher laser fluences F_1 .

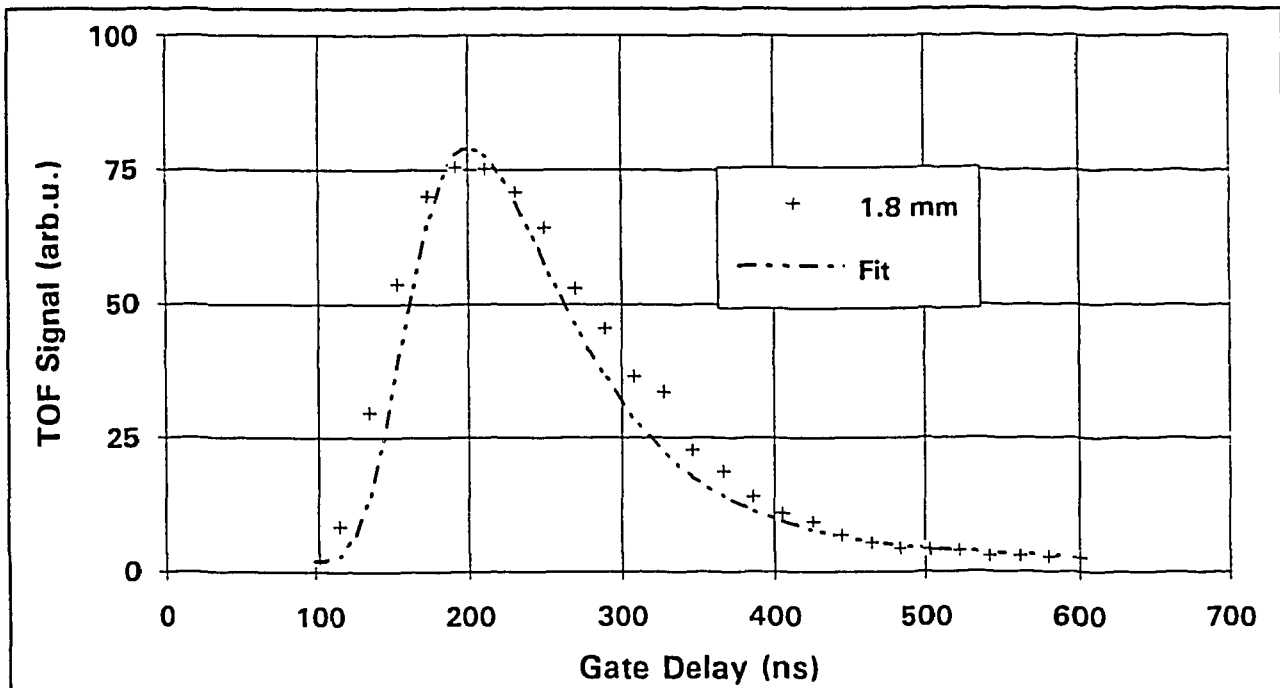


Fig.4: TOF fit by full-range maxwellian function for a height of 1.8 mm above the sample

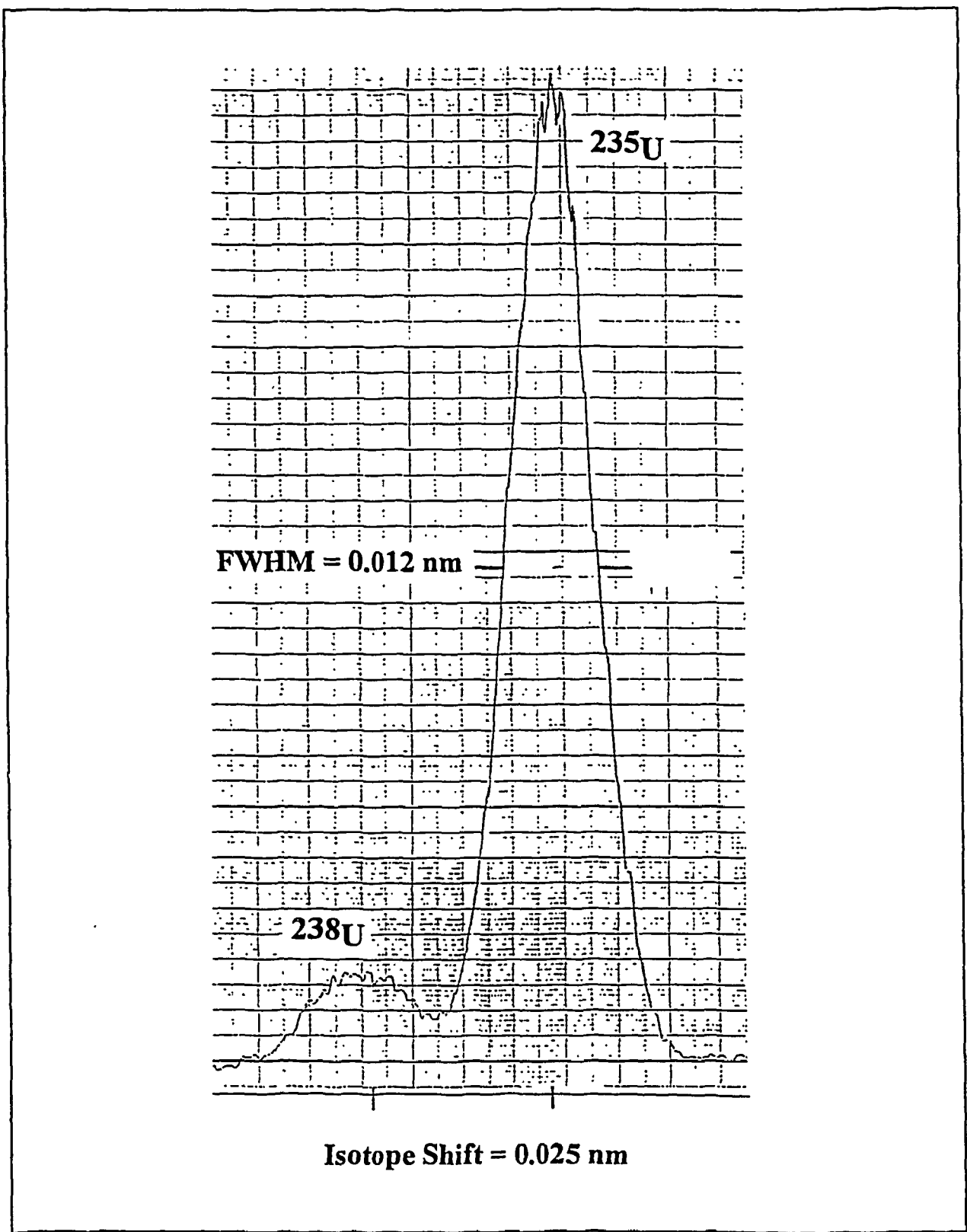


Fig.5: Spectral profile of the U-II 424.437 nm transition for a sample of 93.5 % enriched uranium obtained by means of OES/LPP at reduced pressure

Uranium linewidth measurements are carried out at different observation heights and for different boxcar gate delays. Experiments are done at a pressure of 2×10^{-2} Torr and with a spectral resolution of 5.5×10^{-3} nm. The laser output energy is attenuated to 20 mJ pulse^{-1} (22 J cm^{-2} fluence). We have to point out that FWHM's obtained on uranium are distinctly smaller than the linewidths of the investigated Cu-I transition. Again, Stark broadening is dominant within the first 150 ns after the laser pulse. In the case of uranium, line broadening by Doppler effect is more pronounced than on copper. A best-value of 0.012 nm linewidth is obtained. This result allows to separate the two isotopes ^{235}U and ^{238}U (figure 5).

Samples of enriched uranium are obtained by the process of gas diffusion. At higher enrichment, the amount of ^{234}U (only 0.06 % in natural uranium) is also increasing. The spectrally non-resolved transition of this isotope (law of relative isotope shift [9]) contributes to the measured intensity of the ^{235}U transition and has to be therefore taken into account for the calculation of the isotope ratio $^{235}\text{U} / ^{238}\text{U}$ in the case of enriched samples.

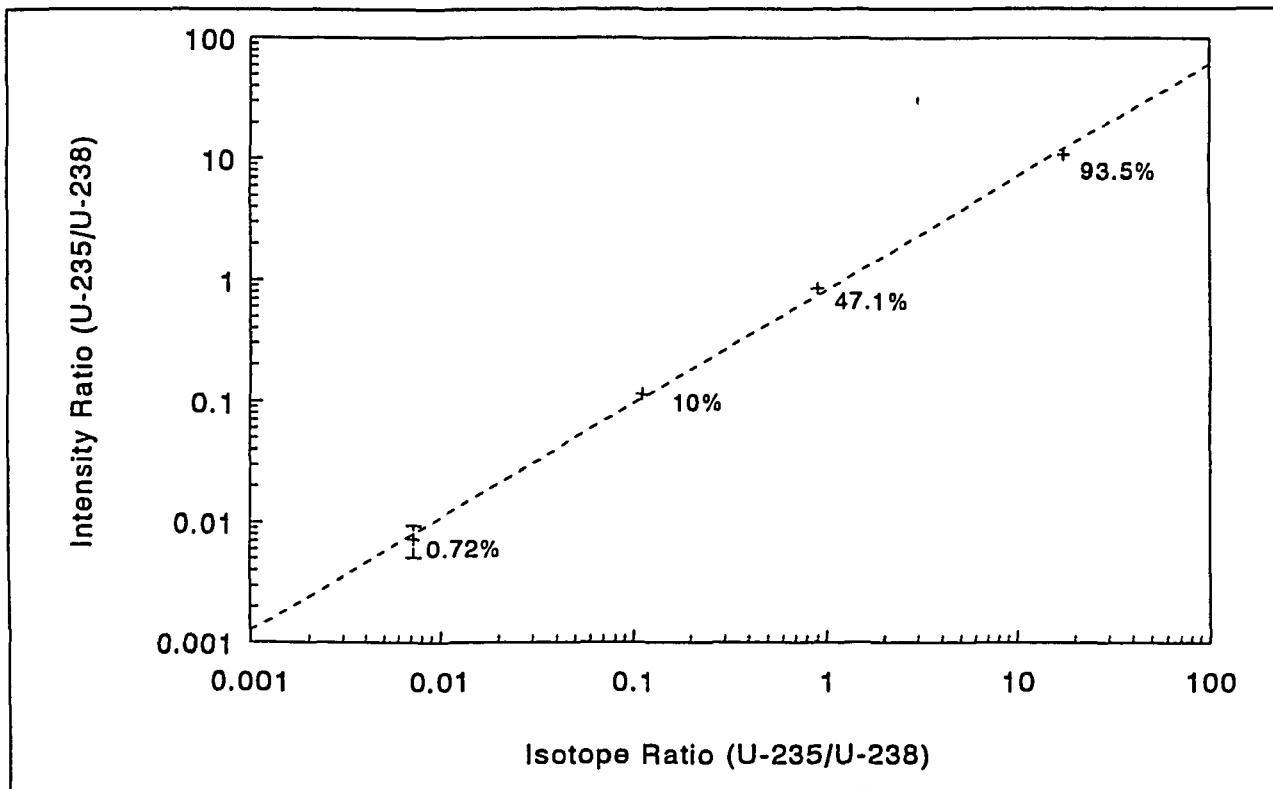


Fig.6: Intensity ratio measurement for isotope ratio determination on uranium by OES/LPP

With increasing enrichment, the precision of the measurement (determination of enrichment on ^{235}U) becomes higher: it increases from 3.8 % for 10 % enriched uranium to

0.3 % for 93.5 % enriched uranium. The natural uranium's isotope ratio of 137.83 disables us to separate more distinctly both isotope transitions on a frequency scale at an optimal spectral resolution of 0.012 nm and a given isotope shift of 0.025 nm for the studied transition. A data acquisition by a multichannel spectrometer should increase the obtained precision of 30 %. This factor presents a limitation of analytical isotope control by this method.

The spectral profiles of the investigated transition U-II 424.437 nm described above show the possibility to obtain an isotopic spectral resolution in a laser-produced plasma under exactly defined experimental conditions. Figure 6 shows the measured line intensity ratio for $^{235}\text{U} / ^{238}\text{U}$ as function of the given isotope ratio.

4. COMPARISON

The method of optical emission spectrometry on a laser-produced plasma and the results of the isotope ratio measurements of uranium are now to be compared with other types of measurements currently used for analytical isotope control.

- Thermal Ionization Mass Spectrometry **TIMS**,
- Inductively Coupled Plasma Mass Spectrometry **ICP/MS**,
- Inductively Coupled Plasma Mass Spectrometry with Laser Ablation **LA-ICP/MS**
- Optical Emission Spectrometry on Inductively Coupled Plasma **OES/ICP**,
- Alpha Spectrometry α ,
- Gamma Spectrometry γ ,
- Glow Discharge Luminescence **GDL**, and
- Glow Discharge Mass Spectrometry **GD/MS**.

The most important point concerns the question, whether a **chemical preparation** of the sample has to be carried out or not. The possibility of an **direct application** (over a distance) in an (industrial) process of the different methods is of equal interest. The question of the **rapidity of the analysis** stands in a direct relation with the two points discussed right now. The use of a method for an **application to establish a cartography** (spatial and in depth) is more or less important for analytical measurements. This ability is given in OES/LPP with a spatial resolution of 0.1 mm² for our experiments. The possibility of an analytical control of **other uranium isotopes** should also be compared. The obtained spectral resolution doesn't allow to control isotopes of uranium other than ^{235}U , ^{238}U by OES/LPP. Another important point in analytical control is the required **precision of the measurements**. After certain

improvements, OES/LPP used for analytical isotope control of uranium should reach a precision of 1 %. A further question concerns the possibility to **determine in a direct way the amount of sample mass** during an analytical measurement of a pellet. This determination is required, if one wants to know the amount of investigated species in the sample.

We want to cite again, in order of importance, the **main advantages of this method**:

- *no chemical preparation,*
- *direct application (over a distance),*
- *rapidity of analysis,*
- *possibility of cartography in 2 dimensions,*

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