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LA-UR--91-409

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Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE HIGH EFFICIENCY RESONANCE IONIZATION MASS SPECTROMETRIC ANALYSIS BY EXTERNAL LASER CAVITY ENHANCEMENT TECHNIQUES

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SUBMITTED TO SPIE OE. LASE 91
Los Angeles, CA
1/20-25/91

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High efficiency resonance ionization mass spectrometric analysis by external laser cavity enhancement techniques

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ABSTRACT

The demand to measure high dynamic range isotope ratios on small samples with resonance ionization mass spectrometry (RIMS) continues to increase. This paper discusses high ionization efficiency methods which can be applied to continuous wave (cw) RIMS to potentially achieve several tens of percent ionization efficiencies for certain elements. The primary technique under development to achieve this is an external laser cavity which can generate very high circulating laser powers.

1. INTRODUCTION

The ability to measure large isotope ratios for rare isotopes with small samples continues to increase.[1-3] Resonance Ionization Mass Spectrometry (RIMS) is one method being explored for this purpose. The major problem which has limited the accomplishment of this task has been the achievement of high overall ionization efficiency simultaneously with good sample utilization.

RIMS is a technique in which lasers are used to selectively excite and subsequently ionize an atom followed by a mass spectrometer for mass sorting and detection. The ionization process may be accomplished in one or more steps, with a photon causing each step of the process. The number of steps is dependent upon the wavelength of the lasers utilized and the ionization potential of the atom in question. If more than one photon is used for the ionization, either real or virtual states may be accessed as intermediate states. The RIMS technique takes advantage of the fact that every element has a unique set of atomic transitions. Therefore, when a laser is tuned to a particular resonant transition of an element of interest obtains complete selectivity is obtained over other elements. In addition, isotopes of the same element have different isotope shifts and fine structure, thus, potentially providing an additional level of selectivity.

Two type of lasers have been applied to isotope analysis by RIMS: pulsed and continuous wave (cw). While pulsed lasers have high peak powers and broad tuning ranges, several characteristics limit their general utility: low duty cycle (low efficiency, potentially solved by kHz repetition rates), pulse pile-up difficulties (limited dynamic range), poor stability (poor precision), and laser pulse spectral and temporal concerns (ratio biases). In contrast, cw lasers offer 100% effective duty cycles, easily controlled laser profiles (spectral, spatial and temporal), as well as excellent power stability. The major obstacle which has precluded the general utility of cw lasers

for RIMS has been available laser power. While there is normally sufficient intensity available to saturate the resonant transition, the efficient promotion of the excited atoms above the ionization potential remains difficult due to the relatively low ionization cross sections.

The primary objective discussed in this paper is the development of a versatile and viable analytical method capable of large dynamic range ratio measurements on sub-nanogram samples. We propose to accomplish this through the development of high ionization efficiency techniques such as an external cavity. High dynamic range measurements ($\leq 1{:}10^5$) have been demonstrated previously with cw RIMS, primarily through its high duty cycle and power stability versus pulsed sources.[3,4] We have also demonstrated that a secondary, non-resonant laser can substantially increase ionization to yield efficiencies of ~0.1% in lutetium[5]. The process of promoting an atom from the excited state to an ion is conducive to the application of a powerful laser such as the argon ion since the ionization cross is typically very small, and thus not susceptible to saturation. However, further large increases in ionization efficiency using more powerful lasers is not tenable since such commercial lasers are currently unavailable.

Our primary effort has centered on significantly increasing signal levels through an external cavity technique. This method has the potential to achieve overall ionization efficiencies of tens of percent for several elements (specifically Th). Such a technique is expected to easily yield a 100-fold increase in coherent circulating laser power. This paper will focus on certain theoretical and experimental aspects of such a system, as well as some of our most recent results.

2. EXPERIMENTAL

Our general cw RIMS experimental set-up has been described previously.[6] Specifically, the external cavity RIMS set-up consists of an Ar^+ laser-pumped standing wave dye laser coupled into an external laser cavity constructed around the source region of a 90° single magnetic sector mass spectrometer (see Figure 1). Our external cavity prototype consists of a 98% reflective input coupler mirror, a ~100% high reflector, a polarization selective element and an active-feedback stabilization system. The cavity optics currently in use are coated for 452 nm light, applicable to lutetium, with the next set of optics scheduled for testing being those appropriate for thorium. Our current configuration consists of an input coupler and a high reflector each with a 50 cm radii of curvature with a cavity length of 50 cm, (i.e. a confocal cavity). Optics with other radii of curvature and other cavity lengths have been successfully tested in our laboratory. The stabilization scheme consists of a high reflector mirror driven by a piezo-electric stack whose drive voltage is generated from an error signal derived from the polarization dependent element.[7] The purpose of the stabilization circuits is to maintain a phase matched condition within the cavity such that the external cavity has maximum build-up or gain (i.e., the length is $n*\lambda/2$).

3. BASIC PRINCIPALS

Although the basic theory in the properties of external laser cavities has been thoroughly discussed previously,[7,8] it is useful to briefly discuss some of the important basic principals and properties involved. The gain function can be described as follows: if the reflectivity of the input coupler is R, and the round-trip attenuation is V, the enhancement factor, E, for the cavity is given by: $E = (1 - R)/(1 - sqrt(RV))^2$. The maximum enhancement occurs when the input coupler reflectivity exactly matches the round-trip attenuation (i.e., $R = V$, such that $E = (1-R)^{-1}$).

The cavity operation can be described in simple terms as follows: the resonant laser output beam is aligned into the input coupler, which passes 2% of the beam into the cavity. Thus, 2% of the laser beam incident on the input coupler is being continuously fed into the cavity with only 2%

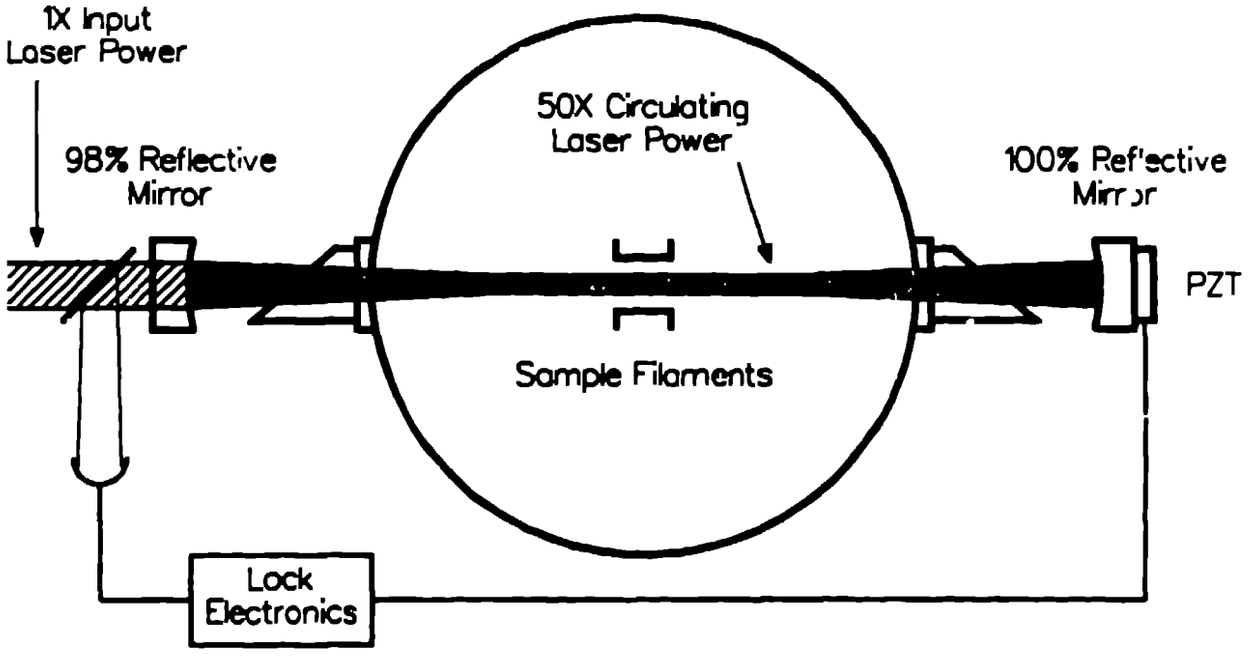

Fig. 1. Mass spectrometer source and external laser cavity configuration to be used in RIMS experiments. With mirror reflectivities shown, a 50-fold circulating laser power increase over the input laser power is calculated.

of that escaping. It becomes clear that this external laser cavity will build up internal circulating power to very high power levels. Imperfect reflecting surfaces and destructive interference reduce actual performance. The former can be optimized by high quality optical coatings; the latter requires the active phase sensitive locking system discussed above.

In addition, several other factors must be controlled and optimized. These include the cavity length, mode matching, and beam waists.[9] Importantly, the capability to vary beam waists allows the optimization of the cavity gain with the atom reservoir for maximum overlap and thus efficiency.

4. RESULTS

We have recently completed prototype testing of the cavity in an unstabilized configuration (i.e., without feedback electronics). Under these conditions, we have demonstrated extremely promising values of an average gain factor of ~20 (corresponding to 4 watts of circulating laser power) and a peak (instantaneous) enhancement of ~45-fold (9 watts). The maximum build up factor is theoretically limited by only the round trip loss and the reflectivities of the input coupler and high reflector mirror. With the newest generation of coatings available for optics, gain factors of ≥1000 should be achievable. Gain factors of ≥100 have been easily achieved [10]

We are currently testing the actively stabilized configuration of the cavity. It has been shown in bench top experiments that the PZT motion is intimately involved in the gain. In addition, the importance of mode matching and variable external cavity beam waists has been verified. Complete actively stabilized operation of the external cavity has not yet been achieved, but we anticipate this in the immediate future. In an active feedback stabilization set-up, we expect to be able to match or exceed the peak enhancement factor already observed, approaching the theoretical value for the set of optics we are currently using, of a 50 fold increase over the input laser power.

5. DISCUSSION

The potential for a two order of magnitude (or more) gain in the circulating laser power and the corresponding increase in ionization efficiency make the external laser cavity approach to RIMS extremely attractive. Figure 2 shows theoretical modeling calculations (similar to ref. 11) of the relative RIMS signal enhancement (ionization efficiency) under various conditions. The plots show the dependence of relative ionization efficiency as a function of laser beam diameter. The lower curve shows this dependence for a single dye laser with 200 mW of power. The other three curves indicate conditions where a 50-fold gain external cavity is utilized for both/either the dye laser and/or argon ion laser.

Amplification of a single laser should lead directly to a $\geq$50-fold improvement in the ionization efficiency. Figure 3 shows a calculational comparison of the sample utilization with and without the benefit of an external cavity.

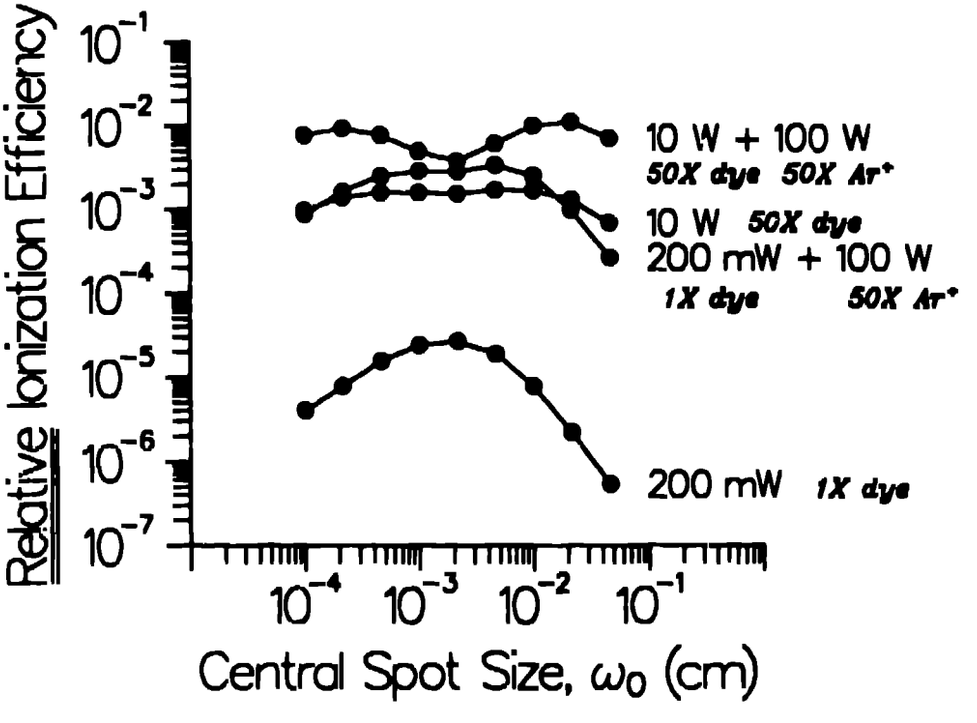

Fig. 2. Detailed calculation of relative ionization efficiencies as a function of beam diameter with differing dye and argon ion laser powers.

From these calculations, the promising results with our unstabilized external cavity and with our current ionization efficiency of ~1% for Th using simple cw RIMS[12] — the utilization of the external cavity could potentially lead to overall ionization efficiencies for Th of several tens of percent. This increased efficiency should allow for sub-nanogram isotopic ratio analyses of thorium at the $5{:}10^6$ level (^{230}Th:^{232}Th) which are critical for internal isochron measurements important for geochronology.[12]

As we have noted, a second laser, such as an Ar^+ ion laser, can also be used for the ionization step.[5] This second laser can also be amplified via another external cavity, which then allows for even greater increases in the the volume of atoms addressed and hence, ionization efficiency. Such increases could lead to ionization efficiencies $\geq$2 orders of magnitude (see Fig. 2) greater than available from single-pass dye configurations. As circulating laser powers continue to increase, saturation conditions will become important; however, this is not necessarily a limitation because the laser beam diameter can be increased. Obviously, there will be some optimum combination of laser power and beam diameter.

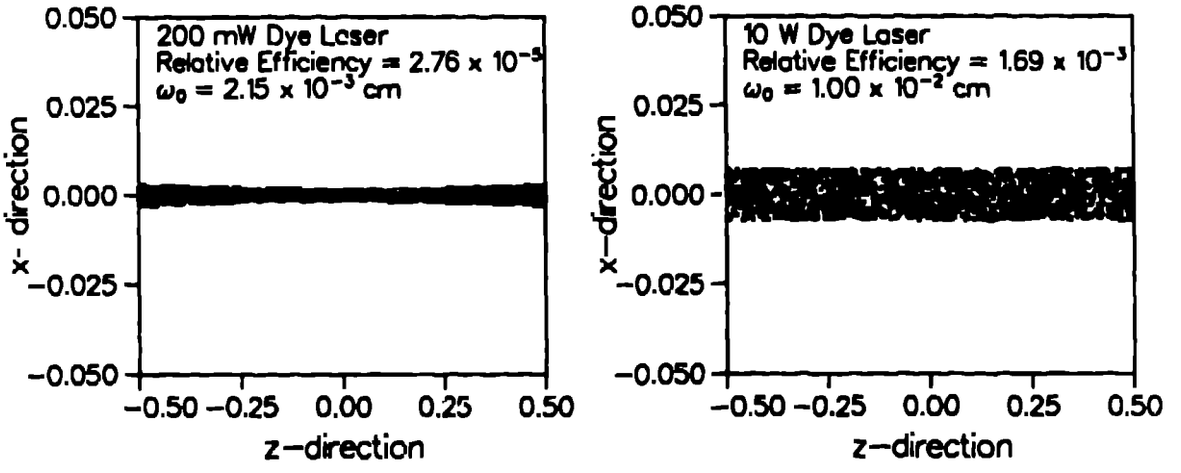

Fig. 3. Ionization calculation showing the comparison in ionization volume both without and with the operation of the external cavity. The x-direction is across the sample filament (cross-section of laser beam) and the z-direction is along the active length of the filament (along the laser beam).

6. SUMMARY

Theoretical calculations and preliminary data have been presented that demonstrate that the utilization of an external laser cavity to boost the circulating laser power leads to substantially increased ionization efficiencies for cw RIMS. An average gain of ~20-fold and an instantaneous gain of ~45-fold have been observed. A gain factor of 100 is expected for a final configuration utilizing a 99% reflective input coupler. Incorporation of the external cavity technique into cw RIMS should lead to ionization efficiencies as high as tens of percent for certain elements. This will largely remove present limitations of cw lasers for RIMS research and analysis.

7. ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy under contract W-7405-ENG-36. Special thanks go to Jim Bergquist of NIST-Boulder for in-depth discussions and assistance in the development of our external cavity.

8. REFERENCES

1. J. D. Blum, M. J. Pellin, W. F. Calaway, C. E. Young, D. M. Gruen, I. D. Hutcheon, and G. J. Wasserburg, "Resonance Ionization Mass Spectrometry of Sputtered Osmium and Rhenium Atoms," Anal. Chem., 62, 209-13, 1990.
2. G. S. Hurst, "Trends in Resonance Ionization Spectroscopy," Resonance Ionization Spectroscopy 1986, eds. G. S. Hurst and C. G. Morgan, 1-4, Inst. of Physics, Bristol, 1987.
3. C. M. Miller, N. S. Nogar, E. C. Apel, and S. W. Downey, "Resonance Ionization Mass Spectrometry at Los Alamos National Laboratory," Resonance Ionization Spectroscopy 1986, eds. G. S. Hurst and C. G. Morgan, 109-14, Inst. of Physics, Bristol, 1987.
4. C. M. Miller, R. Engleman Jr., and R. A. Keller, "Resonance-ionization Mass Spectrometry for High-resolution, Mass-resolved Spectra of Rare Isotopes," J. Opt. Soc. Am. B, 2(9), 1503-9, 1985.
5. B. L. Fearey, D. C. Parent, R. A. Keller, and C. M. Miller, "Secondary, Non-resonant CW Laser Ionization Efficiency Enhancement for Resonance Ionization Mass Spectrometry," Resonance Ionization Spectroscopy 1988, eds. T. B. Lucatorto and J. E. Parks, 263-6, Inst. of Physics, Bristol, 1989.
6. B. L. Fearey, C. M. Miller, M. W. Rowe, J. E. Anderson, and N. S. Nogar, "Pulsed Laser Resonance Mass Spectrometry for Elementally Selective Detection of Lead and Bismuth Mixtures," Anal. Chem., 60, 1786-91, 1988.
7. T. W. Hansch and B. Couillaud, "Laser Frequency Stabilization by Polarization Spectroscopy of a Reflecting Reference Cavity," Opt. Comm., 35(3), 441-4, 1980.
8. J. Helmcke, S. A. Lee, and J. L. Hall, "Dye Laser Spectrometer for Ultrahigh spectral resolution: Design and Performance," Appl. Opt., 21, 1686-94, 1982.
9. A. Corney, Atomic and Laser Spectroscopy, 355, Oxford Univ. Press, Oxford, 1977.
10. J. C. Berquist, private communication.
11. C. M. Miller and N. S. Nogar, "Calculation of Ion Yields in Atomic Multiphoton Ionization Spectroscopy," Anal. Chem., 55, 481-8, 1983.
12. B. L. Fearey, S. G. Johnson, N. S. Nogar, M. T. Murrel, and C. M. Miller, "Thorium RIMS for Geochronological and Geochemical Applications," Resonance Ionization Spectroscopy 1990, in press 1991.