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Short communication

Resonance enhancement of ion signals in direct isotope analysis of metal samples by adopting 2-color resonant laser ablation mass spectrometry

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Abstract

The enhancement of ion signals by the resonant laser ablation (RLA) process was investigated by using a 2-color RLA mass spectrometry for samples containing Pb and Ni. Two laser beams, a second harmonic of Nd:YAG laser (532 nm) and a UV beam of frequency tunable dye laser, were used for either simultaneous ablation by directing both lasers to the target sample or laser ablation followed by a resonant ionization. In both cases, the resonant enhancement of the ion signal was observed, but the mass resolution was much better when two lasers contribute to the laser ablation process by arranging both beams hit the sample at the same position. The enhancement factor was more prominent when the laser power was kept at low. The maximum resonance enhancement was more than 160 times for the Pb case when compared to the non-resonant laser ablation. Several NIST standard reference materials were analyzed by adopting RLA.

Keywords: Resonant laser ablation; Isotope analysis; Laser-induced plasma

1. Introduction

Laser ablation mass spectrometry has been used for the direct isotope analysis of solid sample. But the detection sensitivity of this technique needs to be improved in order to apply for the ultra trace detection. A resonant laser ablation (RLA) is one of the techniques in improving detection sensitivity of laser ablation mass spectrometry owing to the resonance enhancement of ion signals. Since the resonance ionization spectroscopy (RIS) or resonance ionization mass spectrometry (RIMS) has been used for more than two decades in trace detection of isotopes, RLA has been rather easily developed based on the information obtained through the investigations on RIS and RIMS.

The RLA has been applied for the microanalysis of solid materials for some time now [1–12]. The reported investigations include the thin film microanalysis using RLA by Odom and Schuler [1], the trace detection of Al in steel samples by Borthwick et al. [2], the two-photon spectrum of iron and silicon detected by RLA by Eiden and Nogar [3]. Gill et al. investigated the one-color RLA ion trap mass spectrometry for several elements including Co, Ni, Mg, Al, Si, Fe, etc. [4,5]. They were able to detect ~26.5 ppm of a lead content in standard reference materials (SRMs) 494. Aubriet et al. adopted RLA as a tool to investigate a matter transfer during a pulsed-laser deposition experiment [6]. Watanabe et al. thoroughly investigated the RLA, experimentally as well as theoretically [7–10]. Their theoretical model described the RLA process fairly well. The RLA was also applied for the microanalysis of copper by adopting a two-photon resonance ionization with the wavelength of 463.86 nm [11] and an investigation of the internal energy disposal information for Ni by Rothschopf et al. [12]. In most of these papers, either one-color RLA with a two-photon resonance or a two-color RLA arranging one laser for ablation and the other for resonant ionization by dividing one laser beam was adopted. The reported detection sensitivities were dependent on the type of sample, target element and adopted resonant ionization schemes. There are little investigations on the RLA process adopting both lasers on the ablation process.

In the present study, the main focus of the investigation is concentrated on the resonance enhancement of the detection sensitivity by the 2-color RLA processes. We have used two laser beams, 532 nm and a frequency tunable UV laser beam for the RLA process. Two laser beams were arranged for either simultaneous contribution to the ablation process or resonant ablation

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followed by a resonant ionization of the generated laser-induced plasma. The use of 532 nm in ablation process in addition to the frequency tunable laser provides additional flexibility in applying RLA for sample analysis, since most of the pumping lasers for dye lasers or OPOs generate 532 nm which can be used for the ablation process. The time delay between the two laser beams was varied and optimized in order to understand the dynamics of the laser-induced plasma, such as velocity of laser-induced plasma and the effect of UV laser pulses in RLA process. The resonance enhancement of the ion signal for the Pb and Ni samples were obtained as big as 160 times for the Pb case when compared to the ion signal generated by a non-resonant laser ablation. The technique was applied for the trace detection of Pb isotopes and Ni isotopes in several NIST SRMs.

2. Experimental

The experimental setups for laser-ablation and the resonance ionization are described in detail in previous publications [13,14]. In brief, two Nd:YAG lasers, one for the optical pumping of a dye laser and the other for the laser ablation, were used for the two color RLA. The dye laser output was frequency-doubled by using a frequency doubling system (Inrad autotracker II) for the wavelengths, 283.3 nm for Pb and 300.25 nm for Ni, respectively. One of the pumping laser was set as the master trigger for the delay generator and the second Nd:YAG laser. The second laser was frequency-doubled to generate 532 nm and this beam was introduced to the target sample at an angle of 45°. The UV laser was directed at the sample either at 45° (type 1, see also Fig. 1) or parallel to the sample surface (type 2, see also Fig. 1). In the type 1 arrangement both lasers contribute to the ablation process, while only one laser contribute to the ablation process in the type 2 optical arrangement. A home-made time-of-flight mass spectrometer (TOF-MS, linear type) with a flight length of 200 cm was used for the analysis of the generated ions. This TOF-MS system was equipped with an ion source assembly which consisted of eight electrodes, one for a sample mounting and acceleration of the ions, three for an ion optics, and four for an ion deflection in the *X*, *Y* directions. The mass spectrometer was kept under vacuum at $\sim 2 \times 10^{-7}$ Torr. Ions are detected by a dual microchannel plate and the detected signal is amplified by a fast preamplifier before sending it to the digital oscilloscope. The overall experimental scheme is shown in Fig. 1. Metal samples (Pb, Ni) were purchased from Nilaco Co. and used without any further treatment. Adopted SRMs (C-1248, 1155, 1262b) were purchased from NIST.

3. Results and discussion

3.1. RLA-MS with the type 1 laser arrangement

The resonance enhancement of the ion signals in laser ablation mass spectrometry has been a great asset in enhancing the detection sensitivity of the direct isotope analysis technique. The resonance can be achieved by one-step or multi-step, depending on the target element and the available laser wavelength. In the present study on Pb, 2-color RLA was adopted with 532 nm and UV laser. Both laser beams were directed to the same spot at the sample surface with the same angle (type 1 RLA). In this experiment, the size of the laser beam on the target plate was normally optimized as 1.2 mm × 3 mm by defocusing the laser beams. Fig. 2 is the RLA mass spectrum of the Pb obtained by using both the 532 nm and UV laser at two different wavelengths, on and off resonance (283.3 and 282.5 nm), respectively. The average power of 532 nm was adjusted to be relatively low (20 mW) in order to prevent any ion signals from the laser-induced plasma with 532 nm only. The addition of 1.7 mW of UV beam at 282.5 nm along with 532 nm laser generated a very week signal even at non-resonant condition. When the UV laser wavelength was adjusted to the resonant wavelength (283.3 nm) the ion signal was enhanced more than 160 times compared to the ion signal from the non-resonant ablation process.

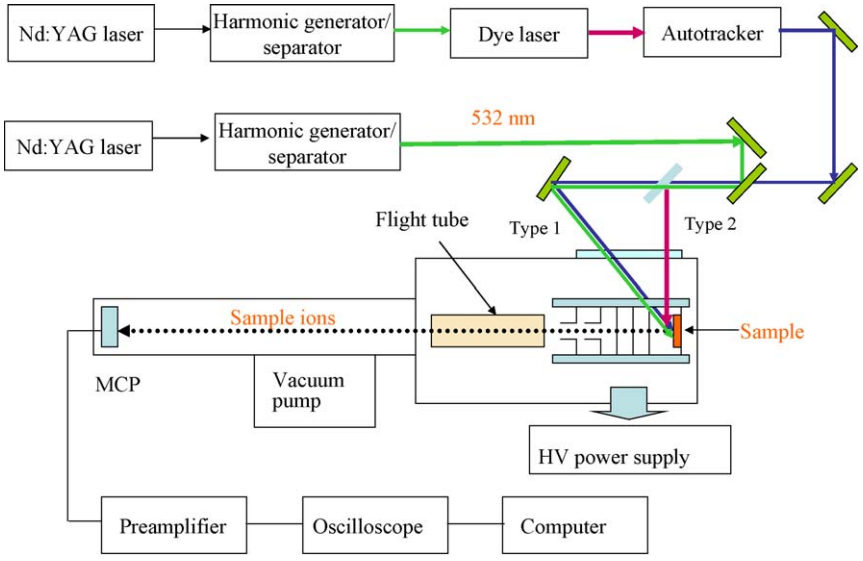

Fig. 1. A schematic diagram of experimental setup for the 2-color resonant laser ablation mass spectrometry.

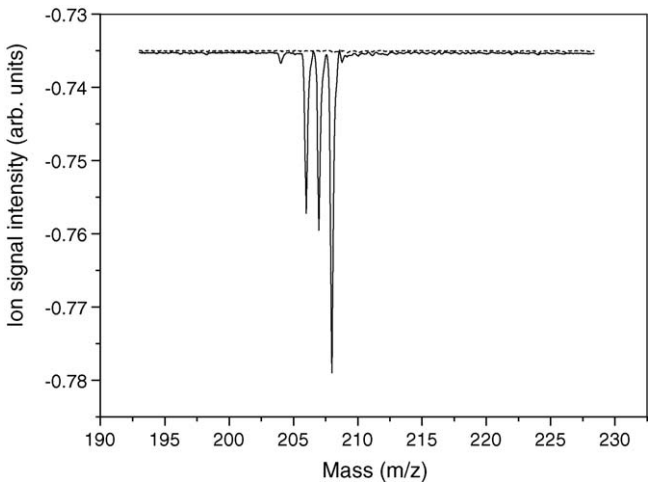

Fig. 2. Time-of-flight mass spectra of the resonant (solid line) and non-resonant (dotted line) laser ablation for Pb. The average laser powers were 20 and 1.7 mW for 532 and 283.3 nm, respectively.

Although the signal enhancement was mainly originated from the resonance effect to the Pb transition, the addition of 532 nm laser beam made the more pronounced signal enhancement. It means the increment of the 532 nm laser energy may greatly increase the ion signal intensity due to the increment of neutral generation by high powered 532 nm. Fig. 3 shows the mass spectra obtained from the non-resonant laser-ablation by 532 nm only (solid line) and the mass spectrum with a 2-color RLA (dotted line). The wavelength of the UV laser was 283.3 nm with a laser power of 1.7 mW, while the average power of 532 nm was increased to 50 mW instead of 20 mW in Fig. 2. The UV laser was operated without an optical delay relative to the 532 nm laser. As can be seen from Fig. 3 the ion signals of Pb isotopes were enhanced by only 17 times. The low enhancement factor at high power of 532 nm laser may be resulted from the fact that 50 mW of 532 nm laser was enough to generate Pb ions without UV laser beam by non-resonant process. It means the enhancement factor became small due to the big intensity of ions

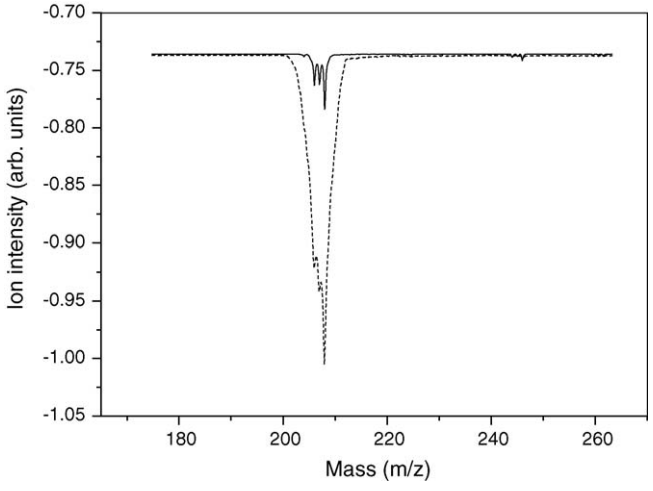

Fig. 3. Laser ablation mass spectra of Pb with a one-color (532 nm only, solid line) and 2-color (532 + 283.3 nm, dotted line) arrangement at average laser power of 50 and 1.7 mW for 532 and 283.3 nm, respectively.

generated by a non-resonant ablation despite of higher overall signal intensity. In addition the mass resolution of the RLA spectrum with higher laser average power was much worse than that with low laser power. Therefore it is evident that the RLA-MS is a much more powerful tool considering mass resolution as well as detection sensitivity when the powers of the two lasers are kept low.

The poor mass resolution, when a high laser power was adopted, can be explained as the space charge effect and higher possibility of collision among species at the ion source region of the time-of-flight (TOF) mass spectrometer. When a high laser power is used for the ablation, more ions can be generated by the laser ablation, but the spatial dispersion of the laser-induced plasma get larger. The larger spatial dispersion may result in a poor mass resolution in time-of-flight mass spectrometer. The number of ions which can be accurately controlled by the mass spectrometer may have some limit depending on the design of the TOF mass spectrometer and voltages applied to the ion extraction electrodes. The ion signal showed a maximum intensity when there was no time delay between the two laser beams. Therefore we can estimate that the both lasers contribute to the ablation process. The RLA mass spectrometry was also investigated for Ni. The adopted resonant wavelength was 300.25 nm for Ni and the resonance enhancement was identified as more than 15 times. But this enhancement factor was much smaller compared to the Pb case due to the different transition efficiencies for adopted resonant transition between Pb and Ni, and different characteristics of elements.

3.2. RLA-MS with the type 2 laser arrangement

In order to verify the role of each laser beam in generating RLA signals, investigation was performed by using 532 nm laser for the ablation and UV laser beam for the resonant ionization of the laser-induced plasma. Fig. 4 is the mass spectrum of Pb with the time delay of 3 μs between the two pulses by adopting the type 2 arrangements. Various clusters of Pb such as Pb_2, Pb_3, PbO, Pb_2O, etc. were observed in this spectrum. A similar

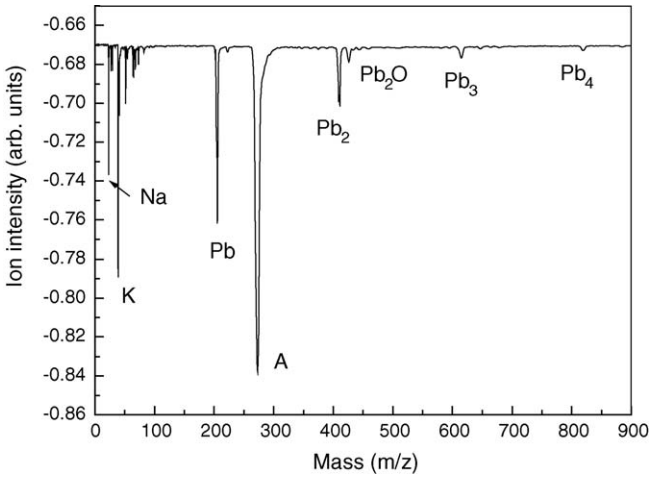

Fig. 4. Laser ablation mass spectrum of the Pb and Pb oxides with the type 2 arrangement of the laser beams.

metal clusters were reported in Ref. [15]. In this figure, a broad mass peak designated as "A" corresponds to the ion signal of Pb generated by the resonant ionization by the UV laser after the laser ablation by 532 nm. This ion signal shows a stronger intensity when compared to the ion peaks generated by the 532 nm laser only, while the mass resolution was considerably deteriorated. The poor mass resolution for peak "A" may be originated from the different electric field condition in ion source region. The electric filed strength between repeller electrode and acceleration electrode of the time-of-flight mass spectrometer which determines the mass resolution may be different for two differently generated Pb ions due to the different position of the ion generation.

The propagation speed of the laser-induced plasma was measured by monitoring ion signals with varying time delay between the two laser beams (532 nm and UV) in type 2 arrangement. The calculated propagation speed of the plasma was ~670 m/s, which corresponded to the supersonic expansion. If the 283.3 nm laser pulse was used for the laser ablation and the time delay was applied for the 532 nm laser beam, no additional enhancement of the ion signal was observed. The lack of signal enhancement by an addition 532 nm photons can be understood due to the low energy of the 532 nm to ionize populated lead neutrals.

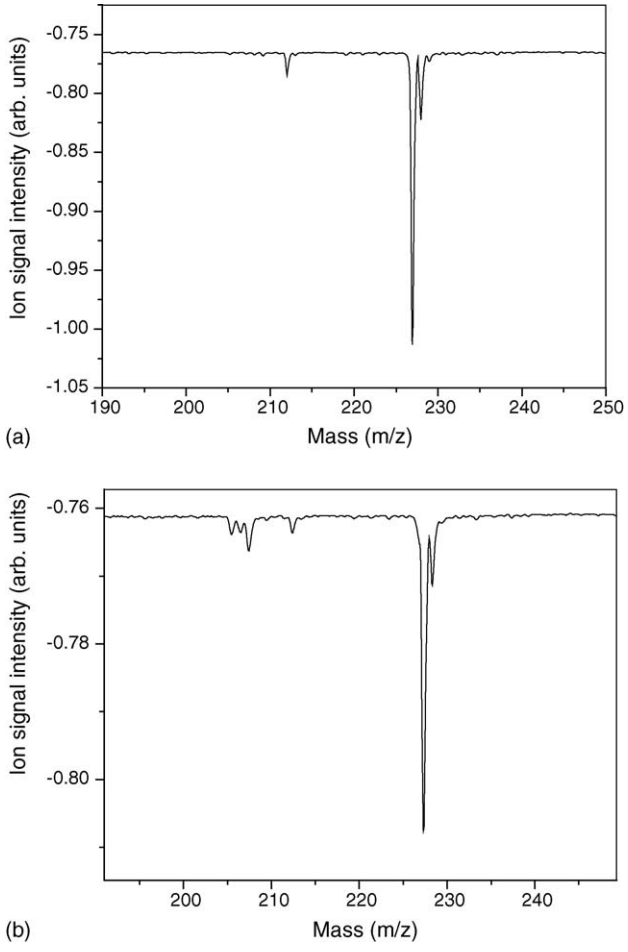

Fig. 5. Detection of a trace amount of Pb in NIST SRM 1262b with a non-resonant LA-MS (a) and a RLA (b). The average power of adopted lasers were 150 and 2 mW for 532 and 283.3 nm, respectively.

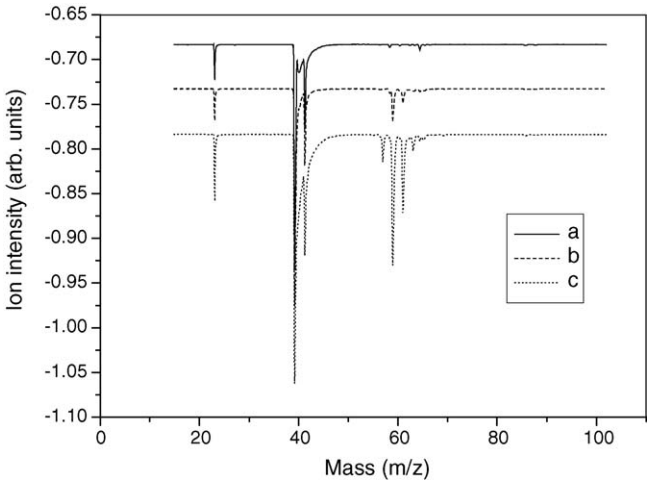

Fig. 6. Detection of trace amount of Ni in NIST SRM C-1248 with various wavelengths. Spectrum is measured using 532 nm only (a), 300.35 nm with 532 nm (b), and 300.25 nm with 532 nm (c).

3.3. Application of RLA-MS for an isotope analysis of trace elements in NIST SRMs

The RLA-MS was applied for the isotope analysis of Ni and Pb for NIST standard samples by adopting type 1 laser ablation. The studied SRMs were 1262b, 1155 and C-1248. Fig. 5 shows the 2-color LA-MS spectra of 1262b using non-resonant (532 nm) ablation (Fig. 5a) and resonant (283.3 and 532 nm) ablation (Fig. 5b). Ion signal of the lead isotopes (0.0004%) were observed only with the 2-color RLA. For 1155 sample, signal enhancement was observed as 12 times when 2-color RLA was adopted with 2 mW of 283.3 nm and 38 mW of 532 nm lasers were adopted for the ablation process. Fig. 6 is the mass spectra of C-1248 using various laser wavelengths. The adopted wavelength was 532 nm only (Fig. 6a), 300.35 and 532 nm (Fig. 6b), and 300.25 and 532 nm (Fig. 6c). The highest signal enhancement was observed when both 300.25 nm corresponding to the resonant transition and 532 nm lasers were adopted for the ablation. The signal enhancement of the Ni isotopes in C-1248 was observed as much as 10 times higher when compared to the non-resonant case.

4. Conclusions

The RLA process was investigated by adopting a 2-color scheme and various metal samples. The enhancement of the ion signal was as high as 160 times for Pb, when compared to the non-resonant case, while approximately 15 times of signal enhancement was observed for Ni. The difference in enhancement factors among elements might be originated from the different transition efficiency of the adopted transitions and the different characteristics of the target samples. The time delay and the sequence of the laser pulses applied for the laser ablation was identified as one of the important parameter in optimizing 2-color RLA process. For the case of Pb, Pb neutrals ablated by 283.3 nm was not ionized by 532 nm photons, while Pb neutrals generated by the laser ablation of 532 nm was easily ionized

by the 283.3 nm laser beam. As a result it was understood that the addition of non-resonant photon during the ablation process might generate more neutrals which can be ionized by the resonant UV photons resulting in an enhancement of ion signal. The developed 2-color RLA-MS was applied for the isotope analysis of the trace elements contained in some NIST SRMs. Further investigation, however, is necessary in order to optimize the analysis conditions, if this technique is adopted for a routine analysis. Nevertheless, the selectivity as well as superior sensitivity of the RLA process may contribute to a direct isotope analysis of solid samples or particles.

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References

[1] R.W. Odom, B. Schuler, Thin Solid Films 154 (1987) 1.
[2] I.S. Borthwick, K.W.D. Ledingham, R.P. Singhal, Spectrochim. Acta Part B 47 (1992) 1259.
[3] G.C. Eiden, N.S. Nogar, Chem. Phys. Lett. 226 (1994) 509.
[4] C.G. Gill, A.W. Garrett, P.H. Hemberger, N.S. Nogar, Spectrochim. Acta Part B 51 (1996) 851.
[5] C.G. Gill, A.W. Garrett, P.H. Hemberger, N.S. Nogar, J. Am. Soc. Mass Spectrom. 7 (1996) 664.
[6] F. Aubriet, N. Chaoui, R. Chety, B. Maunit, E. Millon, J.F. Muller, Appl. Surf. Sci. 186 (2002) 282.
[7] K. Watanabe, K. Hattori, J. Kawarabayashi, T. Iguchi, Spectrochim. Acta Part B 58 (2003) 1163.
[8] K. Watanabe, T. Iguchi, J. Nucl. Sci. Technol. 39 (2002) 312.
[9] K. Watanabe, T. Iguchi, in: J.E. Parks, J.P. Young (Eds.), Resonance Ionizaion Spectroscopy 2000, Proceedings of the 10th International Symposium, American Institute of Physics, 2001, p. 135.
[10] K. Watanabe, T. Iguchi, Appl. Phys. A 69 (Suppl.) (1999) S845.
[11] S.T. Dai, L. Jin, W. Lu,.T. An, L.L. Tai, D.Y. Chen, Appl. Phys. A 69 (Suppl.) (1999) S167.
[12] G. Rothschopf, J. Zoller, R. Lewis, C. Grant, R. Schur, R. Estler, Int. J. Mass. Spectrom. Ion Process. 151 (1995) 167.
[13] K. Song, H. Cha, D.H. Kim, K.H. Min, Bull. Korean Chem. Soc. 25 (2004) 101.
[14] K. Song, D.H. Kim, H. Cha, Y.K. Kim, E.C. Jung, I. Choi, H.S. Yoo, S.W. Oh, Microchem. J. 76 (2004) 95.
[15] A. Hachimi, J.F. Muller, Chem. Phys. Lett. 268 (1997) 485.