Determination of the Isotope Ratio for Metal Samples Using a Laser Ablation/Ionization Time-of-flight Mass Spectrometry

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Received July 11, 2003

The laser ablation/ionization time-of-flight mass spectrometry is applied to the isotopic analysis of solid samples using a home-made instrument. The technique is convenient for solid sample analysis due to the one-step process of vaporization and ionization of the samples. The analyzed samples were lead, cadmium, molybdenum, and ytterbium. To optimize the analytical conditions of the technique, several parameters, such as laser energy, laser wavelength, size of the laser beam on the samples surface, and high voltages applied on the ion source electrodes were varied. Low energy of laser light was necessary to obtain the optimal mass resolution of spectra. The 532 nm light generated mass spectra with the higher signal-to-noise ratio compared with the 355 nm light. The best mass resolution obtained in the present study is ~1,500 for the ytterbium.

Key Words : Laser ablation/ionization, Time-of-flight mass spectrometry, Ytterbium

Introduction

Laser ablation has been one of the useful techniques for sample introduction and as an analytical tool in solid sample analysis.[1-9] Several analytical techniques have been used in isotope analysis of solid samples, such as glow discharge mass spectrometry (GD-MS), laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS) and laser ablation/ionization time-of-flight mass spectrometry (LA-TOF-MS). Glow discharge ionization is a popular ionization method for solid samples, but it holds some disadvantages such as large loss rate of the target samples and the difficulty of local analysis.[10,11] Ion beam ionization has been adopted in SIMS, but the price of the SIMS analysis system is rather expensive and it is characterized by an inherent interference from hydride ions. In comparison with these ionization techniques, laser ablation/ionization has been known as one of the efficient sample introduction methods in mass analysis of the solid samples due to the one-step atomization, vaporization and ionization of the samples.[2,6] In addition, laser ionization can make local analysis possible by ablating a small area of the sample, which is irradiated by laser pulses. Therefore it is very effective in estimating the homogeneity of the solid samples.

The laser ablation/ionization technique has various advantages. Firstly, the ionization process is very simple and low power laser is adequate to generate ions. Secondly, the sample analysis of small amount of sample is possible due to the small loss rate of the sample. Thirdly, ionization is possible for metal samples as well as non-conducting samples. Fourthly, it is possible to analyze the homogeneity of the solid samples by using local analysis. Fifthly, the sample preparation is not necessary and no matrix effect is evident. Due to these advantages, the ICP-MS also has adopted the laser ablation/ionization. But ICP-MS also bears a difficulty in metal sample analysis due to the matrix effect. When the laser ablation/ionization is adapted to the time-of-flight mass spectrometry (TOF-MS), the combined system can show various advantages. Firstly, all mass spectra can be obtained by using only one laser pulse and no influence from the other ions (*e.g.* hydride) is evident. Secondly, the change of the wavelength is not necessary as was the case in RIMS (resonance ionization mass spectrometry)[12-14] Thirdly, no interference effect due to the buffer gas and different matrix as was the case in ICP-MS.

Recently MALDI technology (matrix-assisted laser desorption/ionization) has been rapidly developing and the application to the large molecules as well as synthetic polymers and biological molecules are increased tremendously. The MALDI system uses laser ablation/ionization of the sample matrix and the TOF-MS system. Since the sample is not the metal as is the case of the present study, the ionization mechanism of the MALDI technique may be different from the metal ablation case. However, one-step ionization occurs in both cases.[15-18]

In this paper, the results of the trace analysis for lead, cadmium, molybdenum and ytterbium are presented by using laser ablation/ionization and TOF-MS system. We have measured the basic parameters for laser ablation/ionization and determined an optimal ionization condition. We also demonstrated that isotope analysis of solid samples was performed very rapidly compared with the tedious analytical process by adopting wet chemistry. The measured isotope ratios of the target samples are reasonably agreed to the natural abundance.

Experimental Section

Figure 1 describes a schematic diagram of the experimental setup for laser ablation/ionization TOF-MS system. The 2nd harmonic or 3rd harmonic of the Nd:YAG laser was
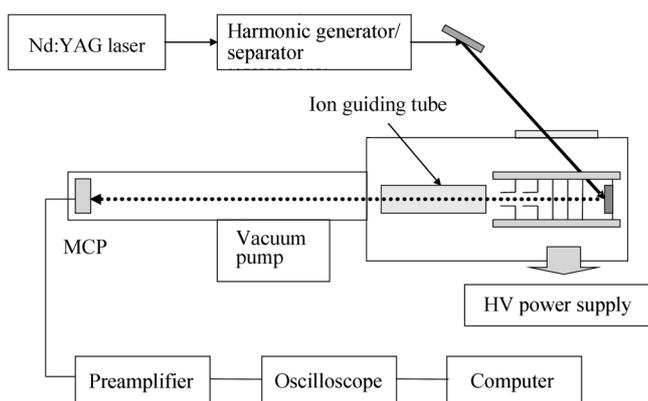
Figure 1. Schematic diagram of the experimental setup for laser ablation/ionization TOF-MS system.

adopted as the laser ablation source and the incident angle of the laser beam to the sample surface was optimized at ~45 degree. The laser beam was focused by a quartz lens (focal length = 25 cm) to make the beam size of 0.5-2 mm of radius depending on the laser energy. Therefore the focal point of the laser beam was located ~5 cm in front of the sample surface. In this configuration, the S/N for ion signals showed the best results.

The TOF-MS system was developed in this laboratory and the details of the ionization region of the system are presented in Figure 2. In general three electrodes were adopted in the Wiley-McLaren type instrument, but one additional electrode was installed in this experimental setup to enhance the mass resolution as well as detection sensitivity. This additional electrode was also used as the holder for sample installation. Therefore once the sample ion was produced, three additional electrodes could act as an ion lens in addition to their use in extraction and acceleration of ions. These electrodes were constructed in rectangular shape and stainless steel tubes were welded to this plate to enhance the collection efficiency of the generated ions. Each electrode was also welded to the stainless steel mesh. In this ion source, four deflection plates were installed to correct the flight path of the ions.

The mass analysis system was constructed with a rectangular chamber (25 cm × 40 cm, aluminum) and a flight tube (1.2 m, stainless steel). The mass chamber was evacuated
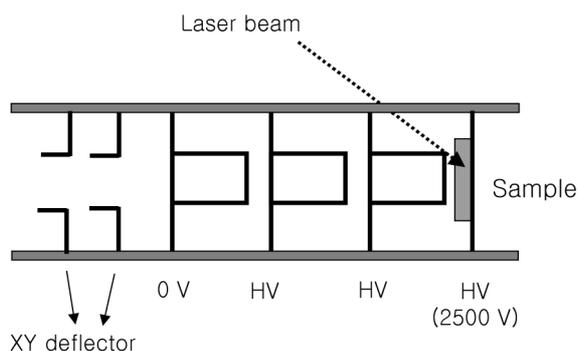
with a turbo molecular pump (Alcatel model 1540) backed by a mechanical pump (Alcatel model 2121) to retain the level of vacuum below 6×10^{-6} torr during the experiment. The generated ions were detected by a dual microchannel plate (Jordan Co. active area: ϕ 18 mm). The ion signal was amplified by a preamplifier (SRS model 244) and analyzed by a digital oscilloscope (Hewlett Packard 53540). This oscilloscope was capable of storing and analyzing mass data. The ion signal was averaged 256 times before storing.

The metal samples (Pb, Cd, Mo, Yb-coated stainless steel) were cut in dimension of 1 cm × 2 cm and installed on the 1st electrode of the ion source of the time-of-flight mass spectrometer (TOF-MS) with a metal clip. The samples were purchased from Goodfellow (England) and Nilaco corporation (Japan) and the surface of each sample was cleaned with ethanol prior to the installation in the vacuum chamber. The ytterbium samples were prepared by coating ytterbium atoms to the stainless steel plates using electro-thermal vaporization.

Results and Discussion

The laser-ablation TOF-MS system has to be optimized before the analysis of metal samples. The basic parameters considered in the laser ablation/ionization process were laser wavelength, laser energy, size of the laser beam, characteristics of the sample surface, etc. Among these parameters, laser wavelength could be one of the important parameters as can be seen following equation.[1]

$$M = 110\left(F_a^{\frac{1}{3}}\right)(10^{14})\lambda^{-\frac{4}{3}}$$

Here M is the loss of the sample mass due to the laser ablation (kg/cm²), F_a is the absorbed laser intensity on the surface (W/cm²), and λ is the laser wavelength. According to this equation, 355 nm is more efficient than 532 nm or 1064 nm laser beam in Nd:YAG laser system. In addition, UV laser is found to be more efficient for the laser ablation.[19-21] In the present study, however, the laser beam had to strike the sample electrode directly, so that the electric noise generated by the laser pulse increased as the laser wavelength decreased. The comparison of mass spectra by changing laser wavelength, 355 nm and 532 nm, is presented in Figure 3. When the 532 nm was adopted for the ablation/ ionization, the signal to noise ratio was better than or at least comparable to the case adopting 355 nm. The mass resolution was comparable in both cases. According to these result, 532 nm is better light source compared to the 355 nm case for our analytical applications. This result indicates that the ablation rate for metal sample might be higher with the shorter wavelength, while the noise generated by laser beam on the sample surface may also increase as the laser wavelength get shorter due to the high electric field on the sample electrode. In most of the previous investigations on the laser ablation, laser ablation has been used for the generation of emission signal (LIBS) or generation of atomic
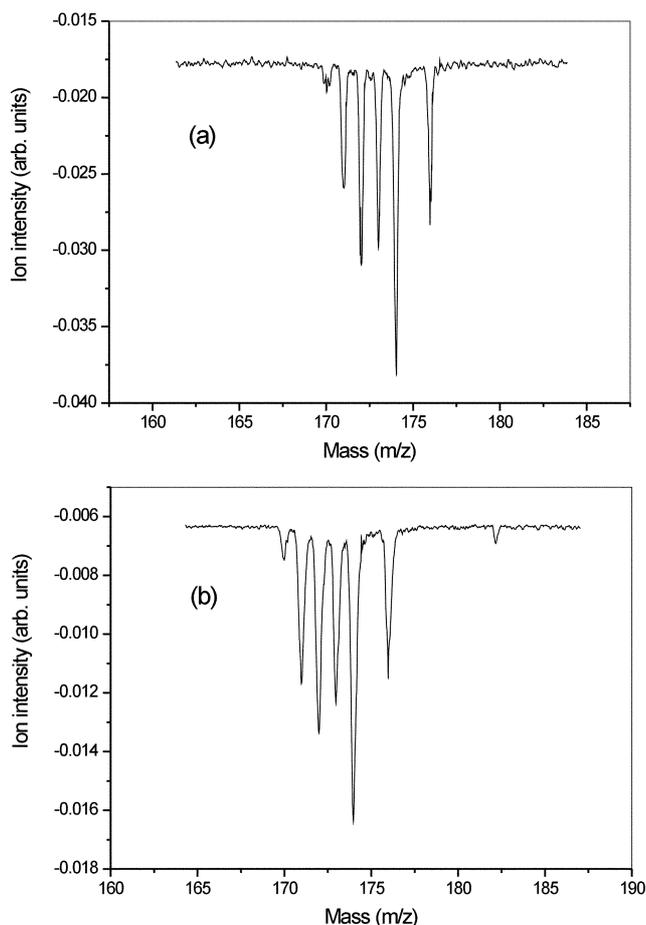

Figure 2. Detailed description of the ion source region adopted for laser ablation/ionization TOF-MS system.

Figure 3. Mass spectrum of Yb ionized by 532 nm (a) and 355 nm (b). The laser energy at 532 nm is 1.2 mJ/pulse, while 355 nm is 0.8 mJ/pulse.
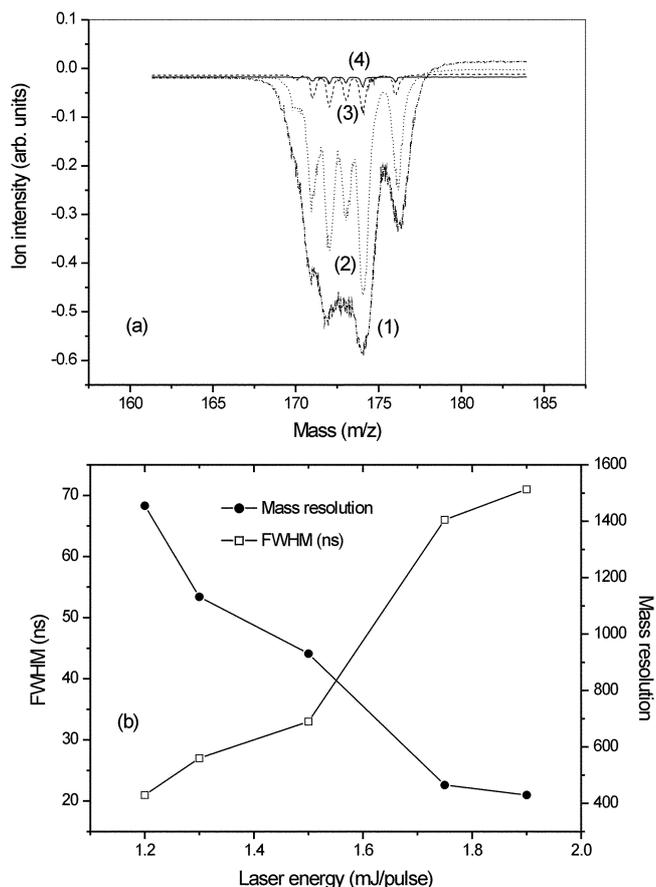

Figure 4. Dependence of ion intensity (a) and mass resolution (b) on the ablation laser energy. The laser energy is (1)2.0 mJ/pulse, (2)1.8 mJ/pulse, (3)1.5 mJ/pulse, (4)1.2 mJ/pulse.

species (LA-ICP-MS). Therefore, higher yield of the ablation product generated higher signal without deteriorating emission signal or mass signal. Since the sample was used as one of electrodes in an ion source in this study, the electrical noise generated by the laser beam during the ablation process may effect greatly to the signal-to-noise ratio. Therefore, the laser energy has to be optimized in order to obtain good signal-to-noise-ratio.

As far as the laser energy is concerned, adopting high laser energy in the ablation process may deteriorate the mass resolution of the system due to the saturation of the ion signal as well as the electrical noise generated by the plasma expansion. The laser energy has to be changed depending upon the characteristics of the samples, such as melting points, hardness, density, etc. If the sample surface is harder than the other samples, more laser energy has to be supplied to obtain the equivalent ion signal. The dependence of the ion signals on the laser power is presented in Figure 4 when the 532 nm was adopted. When the laser energy was 2.0 mJ/pulse, the ion peaks in mass spectrum was saturated, and therefore, the resolution became very poor. When the laser energy is decreased to 1.2 mJ/pulse, the best mass resolution of ~1,500 is obtained. In both cases the size of the laser

beam on the sample surface was ~2.0 mm^2. In most of the laser ablation studies tightly focused laser beam is commonly used.[1,6] In this study, however, lager size of the laser beam produced a better signal-to-noise-ratio, which indicated an optimization of laser energy is important in improving mass resolution of the measured data. But too low laser energy may greatly decrease the ion intensity.

Figure 5 shows the laser ablation/ionization TOF mass spectrum of molybdenum (5-a), lead (5-b) and cadmium (5-c) plates. The spectra show seven isotopes of molybdenum (m/z = 92, 94, 95, 96, 97, 98, 100), four isotopes of lead and six isotopes of cadmium. Two minor isotopes of cadmium were barely observed. The measured isotope ratios for these samples are summarized in Table 1. The measured experimental data agrees reasonably with the natural abundance, but some difference is still evident. The difference between experimental data and natural abundance can be explained as collisions inside the laser-induced plasma and space charge effect. When the laser-induced plasma is generated by a pulsed laser beam, a rich population of the ions, neutrals and electrons are present in the plasma. The dense environment in the plasma can induce the space charge effect, which may deteriorate the correct representation for each element as well as each ion. The discrepancy of the isotope ratio from the natural abundance has been observed in laser ablation/
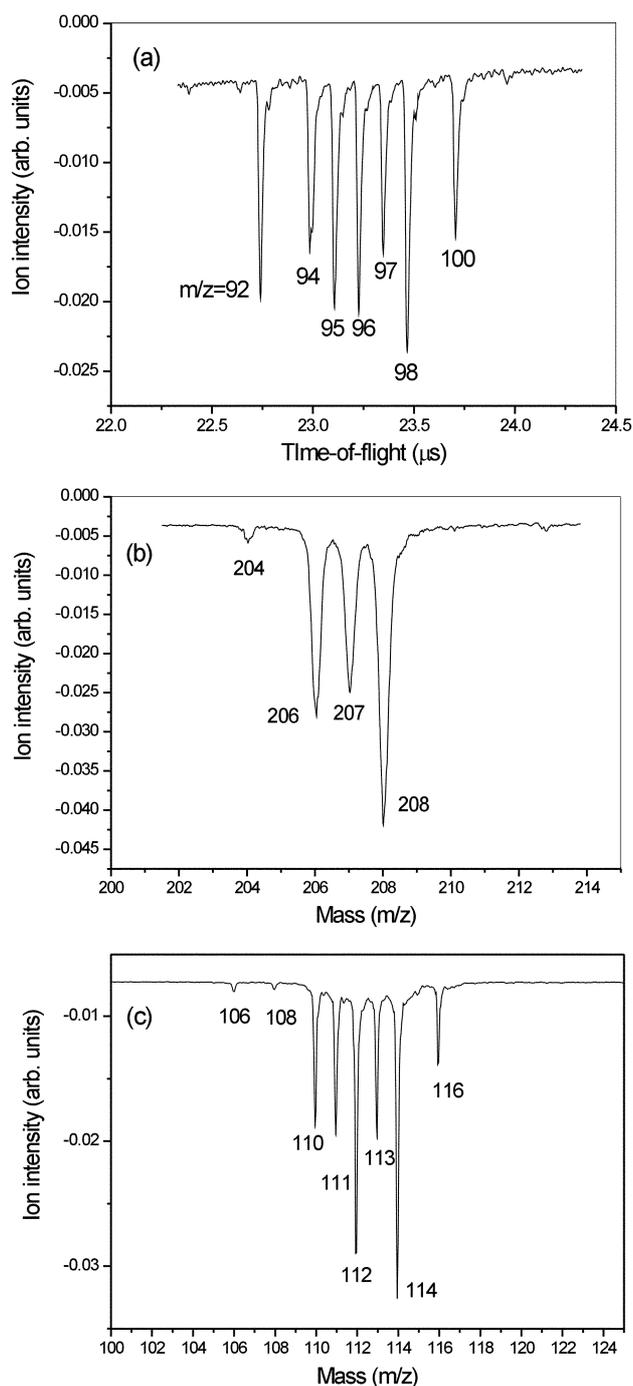
Figure 5. Laser ablation/ionization TOF-MS spectra for molybdenum (5-a), lead (5-b) and cadmium (5-c). The laser energy is 2.5 mJ/pulse and the size of laser beam at the sample surface is 2 mm².

ionization ion trap mass spectrometry. The discrepancy has been explained as the space charge effect.[6]

   The mass spectrum for ytterbium coated on the stainless-steel plate is presented in Figure 6. When the thickness of the coated layers is relatively thin enough to be removed by several laser shots, the stainless steel substrate can be also ablated, and therefore, such elements as Fe, Cr, Ni, etc. are measured in mass spectrum as shown in Figure 6-(a). The

Table 1. Comparison of the experimental data and natural abundance for selected samples

Sample	Mass (m/z)	Measured abundance (%)	Natural abundance (%)
Mo	92	15.6	14.8
	94	10.8	9.3
	95	16.0	15.9
	96	15.3	16.7
	97	10.9	9.6
	98	20.9	24.1
	100	10.5	9.6
Pb	204	1.9	1.4
	206	25.4	24.1
	207	21.5	22.1
	208	51.2	52.4
Cd	106	1.1	1.2
	108	0.8	0.9
	110	12.5	12.4
	111	13.0	12.8
	112	23.3	24
	113	13.6	12.3
	114	28.0	28.8
	116	7.6	7.6
Yb	168	Not detected	0.1
	170	3.9	3.1
	171	16.2	14.3
	172	19.9	21.9
	173	14.4	16.2
	174	30.3	31.7
	176	15.3	12.7

measured isotope ratio for ytterbium agrees reasonably to the natural abundance as shown in Table 1. The error in measuring the isotope ratio is estimated as less than ± 10% comparing to the natural abundance. This result indicates that the determination of trace impurities in solid samples can be easily achieved by adopting the laser ablation TOF mass spectrometry.

Conclusions

   Laser ablation/ionization TOF-MS was employed to analyze the isotopic abundances of solid metal samples quickly and effectively. Plate samples such as cadmium, molybdenum, and ytterbium were analyzed by using laser wavelength of 355 nm and 532 nm. When the laser ionization was adopted, the mass spectra as well as mass resolution were identified to be seriously depending on the laser energy. In optimal conditions, mass resolution of 1,500 was observed for the developed system. The measured isotope ratio for various samples agrees within 10% of the natural abundances. This result indicates that experimental condition for detecting ions generated by laser ablation is very different from the case of generation of atomic species by laser ablation. Further improvement on the ablation
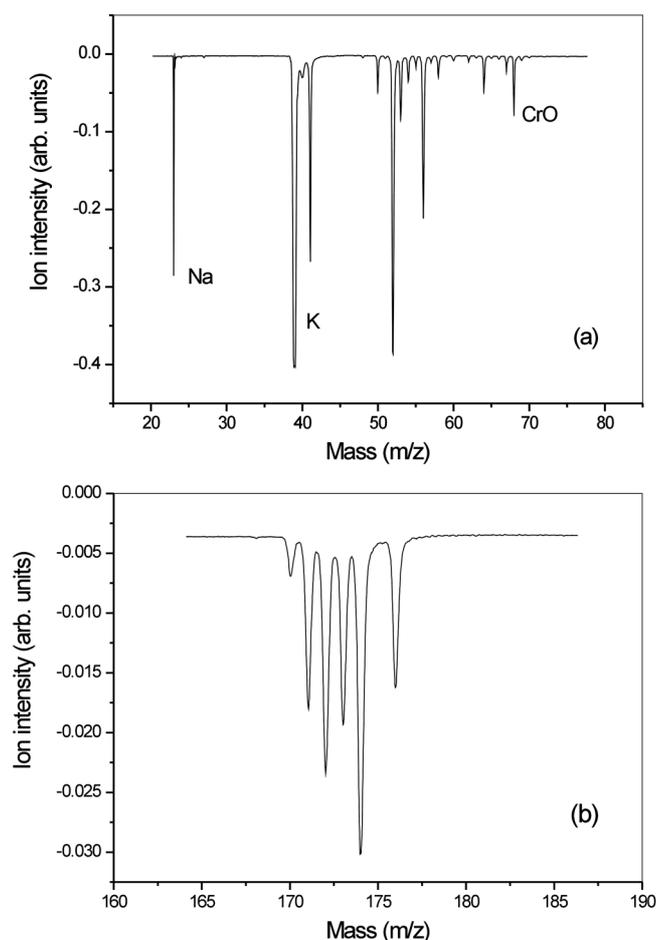
Figure 6. Mass spectra of Yb coated on the stainless steel substrate. Figure 7-(a) shows ion signals generated from the stainless steel, while Figure 7-(b) shows well-resolved mass spectrum of ytterbium. The laser energy is adjusted as to 1.2 mJ/pulse in both spectra.

system as well as the detection system is in progress to enhance the accuracy of the measurement as well as detection sensitivity.

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