

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/41759129>

Two-Dimensional Separation in Laser Ionization Orthogonal Time-of-Flight Mass Spectrometry

ARTICLE in ANALYTICAL CHEMISTRY · MARCH 2010

Impact Factor: 5.64 · DOI: 10.1021/ac902981j · Source: PubMed

CITATIONS

6

READS

32

6 AUTHORS, INCLUDING:



Rongfu Huang

University of Alberta

26 PUBLICATIONS 186 CITATIONS

SEE PROFILE



Lingfeng Li

Xiamen University

13 PUBLICATIONS 104 CITATIONS

SEE PROFILE



Wei Hang

Shanghai University of Finance and Econo...

102 PUBLICATIONS 1,318 CITATIONS

SEE PROFILE



Benli Huang

Xiamen University

93 PUBLICATIONS 1,202 CITATIONS

SEE PROFILE

Two-Dimensional Separation in Laser Ionization Orthogonal Time-of-Flight Mass Spectrometry

Rongfu Huang,[†] Yiming Lin,[†] Lingfeng Li,[†] Wei Hang,^{*,†,‡} Jian He,[§] and Benli Huang[†]

Key Laboratory of Analytical Sciences, College of Chemistry and Chemical Engineering, State Key Laboratory of Marine Environmental Science, and Department of Mechanical and Electrical Engineering, Xiamen University, Xiamen 361005, China

The capabilities of two-dimensional separation using a high irradiance laser ionization orthogonal time-of-flight mass spectrometer (LI-O-TOFMS) were demonstrated in this paper. Ions were separated via their initial kinetic energy in one dimension and their mass-to-charge ratios in the other dimension. Investigation of the transient ion profiles after laser pulses revealed that the separation of analyte ions from multiply charged ions and gas species ions was achieved. Comparison of mass spectra in the normal accumulation mode and in the two-dimensional separation mode indicated that the relative sensitivity coefficients are stable and close to their true values in the two-dimensional separation mode, especially for trace elements that are prone to interference.

Laser ionization mass spectrometry (LIMS) was developed in the 1970s for both analytical and fundamental studies^{1–5} and has become one of the leading technologies for direct solid analysis.^{6–9} Spectra from LIMS suffer less interference compared to spectra from laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) and from glow discharge mass spectrometry (GDMS).^{10–13} Solids can be analyzed by LIMS regardless of the physical property of the sample, provided the laser energy can

be absorbed. This character allows for the analysis of conductors, insulators, bulk or powder samples, and even aerosols.^{4,14,15}

It is well-known that many types of interference exist in elemental mass spectrometry, especially for low mass elements. Multiply charged ions and gas species ions are normally two of the most severe sources of interference in LIMS.^{5,6,16} For example, signal intensities of doubly charged ions are almost equal to the intensities of their singly charged counterparts at an irradiance of $\sim 10^9$ – 10^{10} W/cm² when a traditional high vacuum source is used.^{17,18} Several improvements have been made in recent years, including the use of high laser irradiance ($\sim 10^{10}$ W/cm²) and inert buffer gas (~ 2000 Pa) in the ion source, which provide relatively clear spectra when used with the laser ionization orthogonal time-of-flight mass spectrometer (LI-O-TOFMS).^{14,17,19} These steps reduce interference ions to some extent with optimized instrumental parameters; however, the complete elimination of interference remains impossible. Polyatomic ions including gas species can be effectively dissociated in the ultrahigh temperature environment induced by high laser irradiance; however, multiply charged ions are generated abundantly along with the decrease of polyatomic ions.

In this paper, we propose a two-dimensional separation using a modified LI-O-TOFMS that clearly separates multiply charged ions and gas species ions from analyte ions based on the difference in their kinetic energies and mass-to-charge ratios. It should be noted that an electrostatic energy analyzer in combination with TOFMS can also perform the similar task.^{20,21} However, for the high irradiance laser source, we take full advantage of the orthogonal geometry of the instrument, without using the electrostatic analyzer, to achieve the two-dimensional separation.

* Corresponding author. E-mail: weihang@xmu.edu.cn.

[†] Key Laboratory of Analytical Sciences, College of Chemistry and Chemical Engineering.

[‡] State Key Laboratory of Marine Environmental Science.

[§] Department of Mechanical and Electrical Engineering.

- (1) Klunder, G. L.; Grant, P. M.; Andresen, B. D.; Russo, R. E. *Anal. Chem.* **2004**, *76*, 1249–1256.
- (2) Smith, B. *Trends Anal. Chem.* **2007**, *26*, 60–64.
- (3) Russo, R. E.; Klunder, G. L.; Grant, P.; Andresen, B. D. *Appl. Phys. A: Mater. Sci. Process.* **1999**, *69*, S895–S897.
- (4) Seufert, H. M.; Jochum, K. P. *Fresenius J. Anal. Chem.* **1997**, *359*, 454–457.
- (5) Hang, W. *J. Anal. At. Spectrom.* **2005**, *20*, 301–307.
- (6) Sysoev, A. A.; Sysoev, A. A. *Eur. J. Mass Spectrom.* **2002**, *8*, 213–232.
- (7) Yu, Q.; Chen, L.; Huang, R.; Hang, W.; He, J.; Huang, B. *Trends Anal. Chem.* **2009**, *28*, 1174–1185.
- (8) Schilling, G. D.; Andrade, F. J.; Barnes, J. H.; Sperline, R. P.; Denton, M. B.; Barinaga, C. J.; Koppelaar, D. W.; Hieftje, G. M. *Anal. Chem.* **2007**, *79*, 7662–7668.
- (9) Lin, Y.; Yu, Q.; Huang, R.; Hang, W.; He, J.; Huang, B. *Spectrochim. Acta Part B* **2009**, *64*, 1204–1211.
- (10) Myers, D. P.; Ray, S. J.; Hieftje, G. M. In *Practical Spectroscopy*; Barshick, C. M., Duckworth, D. C., Smith, D. H., Eds.; CRC: Boca Raton, FL, 2000; Vol. 23, pp 447–505.
- (11) Russo, R. E.; Mao, X. L.; Liu, H. C.; Gonzalez, J.; Mao, S. S. *Talanta* **2002**, *57*, 425–451.
- (12) Barnes, J. H. I. V.; Gron, O. A.; Hieftje, G. M. *J. Anal. At. Spectrom.* **2004**, *19*, 1564–1566.

- (13) Harrison, W. W. *J. Anal. At. Spectrom.* **1998**, *13*, 1051–1056.
- (14) He, J.; Huang, R.; Yu, Q.; Lin, Y.; Hang, W.; Huang, B. *J. Mass Spectrom.* **2009**, *44*, 780–785.
- (15) Kokai, F.; Niino, H.; Yabe, A. *Appl. Phys. A: Mater. Sci. Process.* **1998**, *67*, 607–612.
- (16) Vertes, A.; Gijbels, R.; Adams, F., Eds. *Laser ionization mass analysis*; Wiley Interscience: New York, 1993.
- (17) Yu, Q.; Huang, R.; Li, L.; Lin, L.; Hang, W.; He, J.; Huang, B. *Anal. Chem.* **2009**, *81*, 4343–4348.
- (18) Garcia, C. C.; Vadilloa, J. M.; Palancoa, S.; Ruizb, J.; Laserna, J. J. *Spectrochim. Acta Part B* **2001**, *56*, 923–931.
- (19) Peng, D.; He, J.; Yu, Q.; Chen, L.; Hang, W.; Huang, B. *Spectrochim. Acta Part B* **2008**, *63*, 868–874.
- (20) Torrisi, L.; Caridi, F.; Margaroni, D.; Borrielli, A. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2008**, *266*, 308–315.
- (21) Vilppola, J. H.; Tanskanen, P. J.; Barraclough, B. L.; McComas, D. J. *Rev. Sci. Instrum.* **2001**, *72*, 3662–3669.

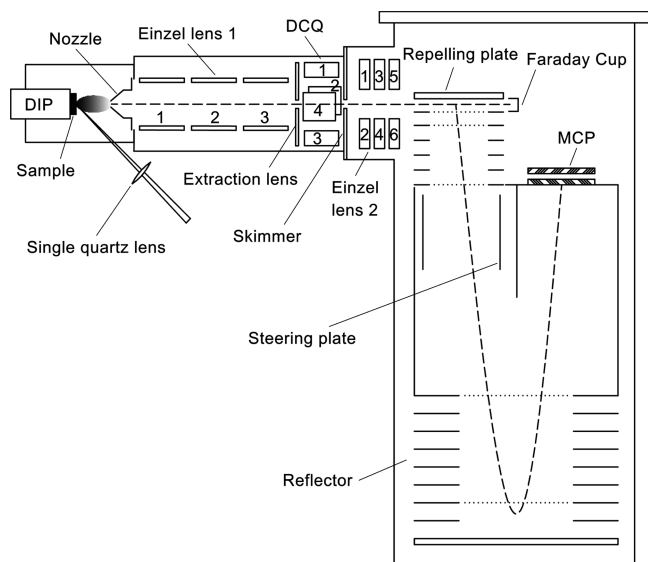


Figure 1. Schematic diagram of the LI-O-TOFMS. DIP: direct insertion probe; DCQ: direct current quadrupole; MCP: micro channel plate.

Table 1. Typical Operating Parameters of the LI-O-TOFMS

Ion Source	
laser wavelength	532 nm
laser pulse frequency	10 Hz
laser irradiance	4×10^{10} W/cm ²
laser spot diameter	50 μ m
laser incident angle	45°
sample to nozzle distance	10 mm
Transportation System	
nozzle	35.2 V
Einzel lens 1 (electrode 1, 2, 3)	−48.0 V, −40.2 V, −122.3 V
extraction lens	−26.2 V
DCQ (electrode 1, 2, 3, 4)	−6.1 V, −5.9 V, −2.4 V, −3.7 V
skimmer	ground
Einzel lens 2 (electrode 1, 2, 5, 6)	ground
Einzel lens 2 (electrode 3, 4)	−17.7 V, −18.7 V
TOF Mass Analyzer	
repelling frequency	10 Hz
repelling pulse length	2 μ s
repelling pulse magnitude	750 V
acceleration potential	−4484 V
steering plate	−4400 V

EXPERIMENTAL SECTION

Figure 1 shows the schematic diagram of the LI-O-TOFMS used in this study, which is an improved version of the system described previously.¹⁹ A set of cylindrical Einzel lens (Einzel lens 1) was employed to replace the previously used two sets of hexapoles that caused mass bias in transmission. Steering plates were added inside the flight tube of the mass analyzer (see Figure 1), such that ions could be detected efficiently while their trajectories were controlled. All vacuum chambers were maintained at high vacuum, and no buffer gas was applied. The typical operating parameters are listed in Table 1.

A series of steel standards (GBW01396, GBW01397, GBW01398, GBW01399, and GBW01400 from National Standard of China) were used in the experiments. Before ablation, samples were cut into disks of about 6 mm in diameter and 1.5 mm in thickness before being immobilized on top of the direct insertion probe (DIP) using kapton tape. The concentrations of iron in the

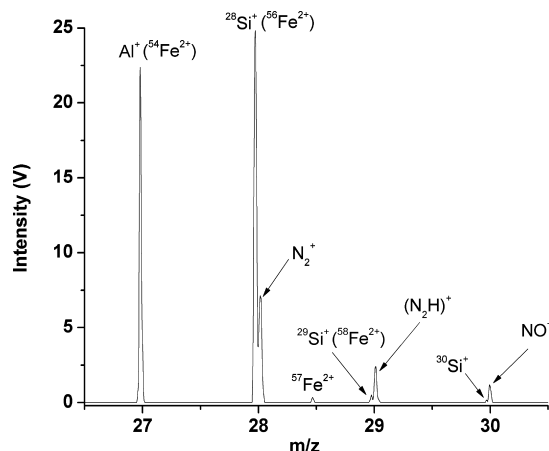


Figure 2. Typical integrated mass spectrum for the steel standard GBW01396.

standard series of GBW01396-GBW01400 were 90.78%, 90.75%, 90.10%, 90.52%, and 91.94% (in wt %), respectively.

Instead of the previous CFD-TDC recording system, we used a high-speed oscilloscope (model 42Xs, 2.5 Gs/s, Lecroy) to record the spectrum induced by a single laser pulse. Every integrated mass spectrum was the accumulation of 100 single mass spectra induced by 100 laser pulses.

RESULTS AND DISCUSSION

It is clear that the unity of ionization fractions can be obtained for most elements with a laser irradiance of 10^9 – 10^{11} W/cm², since nearly all elements are ionized in the plasma core where the temperature can be as high as 10 000–50 000 K.¹⁶ The generation of multiply charged ions, especially the abundant multiply charged ions of matrix elements, is unavoidable under high-irradiance conditions and could result in severe interference in the spectra. As a result, special considerations need to be taken to remove this interference if quantitative measurements are required. As previously reported, by introducing inert buffer gas into the ion source, collisional recombination can effectively decrease the population of multiply charged ions up to 2 orders of magnitude;¹⁷ however, the interference could still be severe if peaks of multiply charged ions and trace element ions overlap one another.

Another source of severe interference in LIMS spectra comes from gas species, which could be introduced by the residual air in the ion source chamber and the gas adsorbed on the microstructure of the sample surface. High laser irradiance and collisional dissociation are common methods to reduce interference gas species and related polyatomic ions; however, high laser irradiance is known to generate multiply charged ions,¹⁷ and both of these methods fail to completely remove the interferential gas species.^{17,22} In general, the nature of interference ions dictates that they could never be eliminated completely by varying only the instrument parameters.

Figure 2 shows a typical integrated mass spectrum for the steel standard GBW01396. Usually, in the mass range that gas species interference appears, the larger the atomic weight, the larger is

(22) Huang, R.; Yu, Q.; Tong, Q.; Hang, W.; He, J.; Huang, B. *Spectrochim. Acta Part B* 2009, 64, 255–261.

Table 2. Theoretical and Measured Ion Weights from the Spectra Shown in Figure 3

nominal mass	ions	theoretical mass (amu)	measured mass (amu) (From Figure 3)	ion type
27	Al ⁺	26.982	26.980	element in sample
	⁵⁴ Fe ²⁺	26.970	26.973	multiply charged ions
28	²⁸ Si ⁺	27.977	27.977	element in sample
	⁵⁶ Fe ²⁺	27.967	27.968	multiply charged ions
	N ₂ ⁺	28.006	28.004	gas species
28.5	⁵⁷ Fe ²⁺	28.468	28.466	multiply charged ions
29	²⁹ Si ⁺	28.976	28.976	element in sample
	⁵⁸ Fe ²⁺	28.967	28.970	multiply charged ions
	N ₂ H ⁺	29.014	29.011	gas species
30	³⁰ Si ⁺	29.974	29.969	element in sample
	NO ⁺	29.998	29.996	gas species

Table 3. RSCs of Al and Si in the Steel Standard Series GBW01396-GBW01400

elements	sample	concentration (%)	RSC (accumulation mode)	RSC (two dimensional separation mode)
Al	GBW01396	0.858	1.97 ± 0.20	1.77 ± 0.16
	GBW01397	0.108	2.29 ± 0.18	1.84 ± 0.19
	GBW01398	0.027	3.48 ± 0.31	2.05 ± 0.24
	GBW01399	1.11	2.33 ± 0.23	2.13 ± 0.17
	GBW01400	0.704	2.55 ± 0.29	2.02 ± 0.18
Si	GBW01396	0.966	3.20 ± 0.49	0.62 ± 0.08
	GBW01397	1.1	2.12 ± 0.38	0.62 ± 0.09
	GBW01398	2.14	1.39 ± 0.15	0.52 ± 0.07
	GBW01399	0.089	23.67 ± 4.53	0.78 ± 0.10
	GBW01400	0.729	4.63 ± 0.65	0.65 ± 0.07

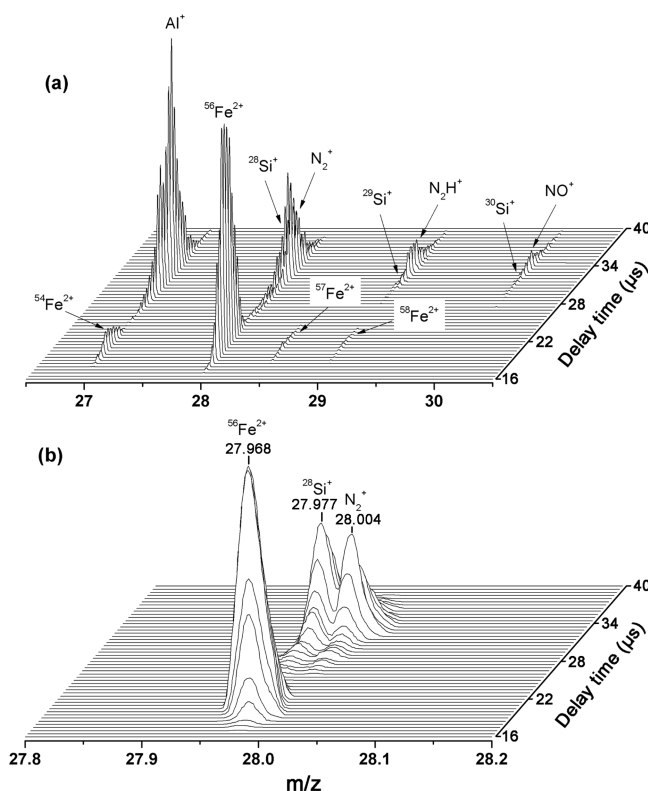


Figure 3. Transient ion profile after a single pulse from the steel standard GBW01396 at (a) 26.5–30.5 amu and (b) 27.8–28.2 amu.

the mass defect. As a result, the following weight sequence always exists: multiply charged ions \approx analyte ions < gas species ions (see Table 2). The m/z difference between the analyte ion and the gas species ion is large enough (e.g., 0.039 amu between ²⁸Si⁺ and N₂⁺) to be resolved by the TOF analyzer with a moderate resolving power (e.g., \sim 1400 at mass 28); while the slight mass difference between the analyte ion and its multiply charged ion (e.g., 0.010 amu between ⁵⁶Fe²⁺ and ²⁸Si⁺) will not be resolved unless a high resolution mass analyzer is employed (resolving power of \sim 5600 at mass 28 for the separation).^{19,23}

Figure 3 shows the transient ion profile for the mass range of (a) 26.5–30.5 amu and (b) 27.8–28.2 amu. The delay time represents the trigger time difference between the laser pulse and

the repelling pulse applied to the repelling plate. The flight time of ions from the ion source to the repelling region depends on the ion kinetic energy and the mass-to-charge ratio. On the basis of Figure 3a, it is obvious that the mass-to-charge ratio has little effect on the ion separation from the source to the repelling region, while the initial kinetic energy of ions plays the dominant role, consistent with previous reports.^{24,25} It appears that higher charge states of ions result in an increase in kinetic energy, which can be explained by the fact that the acceleration of ions is proportional to their charges in the plasma.²⁶ As a result, transient ion profiles of ⁵⁴Fe²⁺, ⁵⁶Fe²⁺, and ⁵⁸Fe²⁺ were separated completely from Al⁺, ²⁸Si⁺, and ²⁹Si⁺. This observation shows that the large difference of the initial kinetic energy between singly charged and doubly charged ions allows for complete separation. Moreover, the enlarged diagram (Figure 3b) shows a 68% separation of the peak representing ²⁸Si⁺ from the peak representing the gas species ion N₂⁺. The separation percentage is dictated by the resolution power of the TOF mass analyzer. Separations of 78% and 72% were also achieved for peak pairs of ²⁹Si⁺/N₂H⁺ and ³⁰Si⁺/NO⁺, respectively. The separation percentage (SP) of two adjacent peaks is defined as:²⁷

$$SP = \frac{|M1 - M2|}{w1 + w2} \quad (1)$$

where $M1$ and $M2$ are exact masses of two peaks, $w1$ and $w2$ are their full-width at half-maximum. With two-dimensional separation via kinetic energy and mass-to-charge ratio, singly charged analyte ions can be separated from the interference caused by multiply charged ions and gas species ions. Measured masses of ions are clarified in Table 2, and their signal intensities can be accurately determined.

In order to verify the practicality of the two-dimensional separation method, the steel standard series GBW01396-GBW01400 was used in the experiment, and the relative sensitivity coefficients (RSC) for Si and Al were calculated (see Table 3). Chromium was

(24) Srivastava, S. N.; Sinha, B. K.; Rohr, K. *J. Phys. D: Appl. Phys.* **2005**, *38*, 3643–3653.

(25) Thum-Jaeger, A.; Sinha, B. K.; Rohr, K. *P. Phys. Rev. E* **2001**, *63*, 016405/016401–016405/016410.

(26) Srivastava, S. N.; Sinha, B. K.; Rohr, K. *P. J. Phys. B: At., Mol. Opt. Phys.* **2006**, *39*, 3073–3086.

(27) Ahuja, S.; Jespersen, N. D., Eds. *Modern instrumental analysis*; Elsevier: Amsterdam, 2006.

(23) Becker, J. S.; Dietze, H. J. *Spectrochim. Acta Part B* **1998**, *53*, 1475–1506.

used as the reference due to its suitable concentration. Isotopes of ^{28}Si and ^{52}Cr were chosen for the RSC calculation because of their high abundances. The RSCs of Al and Si showed high values and large variations in normal accumulation mode, as well as severe interference when the analyte element concentration was low (e.g., $\text{RSC}_{\text{Si}} = 23.67$ for GBW01399 due to the intense $^{56}\text{Fe}^{2+}$ interference and low Si concentration).

The accumulation mode is a routine data acquisition method for TOF mass analyzer, which accumulates all spectra recorded to achieve a high S/N ratio. This mode is inclined to be used for the continuous ion source. However, for a pulsed laser plasma source, two-dimensional separation mode can separate the multiply charged ion interferences from the elemental signals, as shown in Figure 3. Thus, the RSC values for Al and Si were lower and more stable, with variations of 10% and 15%, respectively, compared to 23% and 134% in regular accumulation mode. RSC values for analyte ions free of interference are important for quantitative analysis, especially for the standardless quantitation capability of LI-O-TOFMS. In addition, it is worth noting that besides the multiply charged ions from matrix elements discussed in this paper, multiply charged ions from other elements could also exist in the LIMS spectrum (data not shown). These interferential ions could also be eliminated using the same methodology.

CONCLUSION

The capabilities of two-dimensional separation using LI-O-TOFMS were demonstrated in this paper. Ions were separated via their initial kinetic energy in one dimension and their mass-to-charge ratios in the other dimension. The quasi-simultaneous advantage of TOF detection was inevitably affected, but a clear separation of analyte ions from gas species and multiply charged ions was achieved. Analysis of RSCs from Al and Si in a series of steel standards revealed that the use of LI-O-TOFMS in two-dimensional mode resulted in an improved accuracy and stability of the relative sensitivity, compared to the regular accumulation mode. This methodology has proven to be a promising alternative not only for direct quantitative analysis but also for semiquantitative analysis of solids without standard measurement and calibration procedures.

ACKNOWLEDGMENT

Financial support from the National 863 program, Natural Science Foundation of China, and Fujian Province Department of Science and Technology are highly acknowledged.

Received for review December 29, 2009. Accepted February 25, 2010.

AC902981J