Analytical Efficacy of a Gas Mixer and Stabilizer for Laser Ablation ICP Mass Spectrometry

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ABSTRACT: The analytical efficacy of five gas mixers and five stabilizers on signal stabilization and washout time obtained for laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) was evaluated in the present study. In the case of gas mixers examined, a total of 95 patterns of their attitudes as well as different directions of the gas flows were examined, and it was found that the signal variation and the washout time were strongly dependent on these factors. Even in a simple Y-shaped fitting (Y-mixer), signal stability and washout time had large variations with respect to its different attitudes as well as gas flow directions. The shortest washout time for each gas mixer was almost the same ranging from 1.0 to 1.2 s. The signal variations observed were 11–15% of relative standard deviation (RSD) under optimum conditions for each gas mixer. The optimum condition of a Y-mixer for LA-ICPMS represented 11% RSD and 1.0 s for signal variation and washout time, respectively. In the case of stabilizers examined, almost all stabilizers improved signal variations from 11 to 3.0–9.3%, but washout times became longer than those of the only Y-mixer from 1.0 to 1.2–8.9 s. The important thing is that the signal stability and the washout time are trade-off correlations for gas mixers and stabilizers. A suitable gas mixer or a stabilizer on the trade-off line can be selected with respect to different applications. It was also observed that variations of both signal stability and washout time correlated with the volume of stabilizers despite their different inner structures; that is, a stable signal and longer washout time seemed to be observed when the volume of the chamber became larger. This suggested that the signal stabilization obtained by stabilizers was ascribable to not only elimination of larger particles from laser ablation but also particle mixing effect, which compensated signal variation.

INTRODUCTION

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is widely used for the determination of major and trace elements as well as isotope ratios in solid materials since 1980s.1 The solid material is usually ablated by pulsed laser in a sampling cell, and the laser-generated particles are brought into an ICP mass spectrometer by a carrier gas of helium (He), with mixed argon (Ar) gas in front of the ICP, at an atmospheric pressure. It allows a flexible design for sample introduction system composed of a sampling cell, a transport tube, a gas mixer such as a gas-mixing device, and a stabilizer such as either a static mixer or a signal smoothing device. It is widely recognized that He gas is useful for carrier gas of LA-ICPMS, which can generate smaller size of particles from sampling cell by pulsed laser ablation.2 The smaller particles with narrower size distribution are also very important for stable and precise analysis by LA-ICPMS, which contribute to the stable signals detected by ICPMS because of their stable dissociation, atomization, and ionization in the ICP.

Recently, applications for LA-ICPMS have been becoming much broader such as elemental mapping technique for geological, biological, and industrial materials. Therefore, rapid washout time of LA system is very important to obtain higher spatial resolution and faster ICP-MS measurements for elemental mapping including line scan measurement, as well as a large number of sample measurements. Müller et al. (2009)3 introduced a new designed two-volume sampling cell to achieve rapid washout time (<1.5 s for 99% signal decay). Hence, the washout time of sampling cell has been improved in the past decade, and two-volume cell is commonly adopted for commercial LA systems.

It is also recognized that Ar gas should be mixed into the He carrier gas to stabilize the ICP. In order to mix the Ar and He carrier gases, T- or Y-shaped fittings are commonly used as a gas mixer because of their usability. It was considered that the acceptable washout time could be obtained; however, these gas mixers might influence on a signal stability because they led pressure differences from the mixed gases with different flow
rates. On the other hand, a coaxial gas mixer was less affected by pressure differences between these two gas flows, and it was expected to maintain a laminar gas flow compared to the use of T- or Y-shaped fittings, which could contribute to the stable signal.\(^6\) Attitudes of these gas mixers and the different directions of the gas flows might also influence the signal stability and the washout time; however, these concerning factors have also not been examined in detail to optimize its signal stability and washout time.

Another approach for signal stabilization of laser-generated particles is the use of a stabilizer which is connected to a sample transport tube additionally with the gas mixer between the sampling cell of the LA system and the ICP mass spectrometer. Tunheng and Hirata (2004)\(^5\) developed a baffled-type stabilizer which also acted as the “particle filter” to eliminate larger size particles from laser ablation. This stabilizer obviously improved the signal stability, even though the washout time became longer (about 10–20 s). Hu et al. (2012)\(^6\) developed a wire-type stabilizer, and improved washout time with “particle filter” effect could be obtained. The washout time of the stabilizer was about 5 s for 99% signal decay.\(^6\) Recently, a squid-type stabilizer was also demonstrated, and 99% signal decay as washout time was obtained within 1.5 s.\(^7,8\)

Although the signal stability and the washout time are both important for LA-ICPMS, these two factors are always conflicting. In order to find reasonable and compromised utilization of gas mixers and stabilizers for LA-ICPMS, it is important to understand their properties.

From these points of view, the analytical efficiency of a gas mixer and a stabilizer for LA-ICPMS was evaluated especially for both signal stability and washout time in the present study. Here, we examined five gas mixers and five stabilizers and evaluated their analytical efficacy in detail to understand their characteristics as well as to suggest their reasonable and effective utilization with respect to LA-ICPMS.

### RESULTS

**Signal Stability and Washout Time from Gas Mixers Coupled with LA-ICPMS.** The signal stability and washout time for five gas mixers with a total of 95 patterns of the connections of gas lines and attitudes were evaluated. Details of each gas mixer are mentioned in the Experimental Section. Time-resolved analysis (TRA) profiles of the Y-mixer (15 patterns, Figure 1a) and E-mixer (30 patterns, Figure 1b) showed a trapezoidal shape. Signal variation and washout time of each TRA profile were calculated and are indicated in Table 1.

Simple gas mixers such as T-, Y-, and N-mixers showed smaller variations of washout time (1.0–1.6 s) compared to those of complicated gas mixers (1.1–5.7 s for C- and E-mixers). However, the shortest washout time for each gas mixer, which could be considered under their optimal operating conditions, was almost the same ranging from 1.0 to 1.2 s for all gas mixers (Table 1). The signal variation of the gas mixers varied greatly because of different connections of the gas lines and attitudes of the gas mixers. Even in simple T-, Y-, and N-mixers, TRA profiles showed large variations, and the ranges of signal variations observed were 13–46, 11–21, and 15–26%, respectively, as listed in Table 1. The highest stability (11%) and fastest washout time (1.0 s) were obtained by Ya1 connection. The TRA profile of Ya1 certainly represented a stable top-hat line and a steep down-slope (Figure 1a).

The C-mixer was originally designed as “Ca” connection to accomplish a laminar flow. The signal variation and the washout time of the “Ca” connection were 18–32% and 1.1–1.6 s, respectively, as indicated in Table 1. However, these values were not always better than those of the other connections. The best performance was seemed to be obtained by “CF” connection (the signal variation and the washout time were 13–16% and 1.3–1.5 s, respectively), as could be seen in Table 1 and Figure 2.

Different connections and attitudes for the E-mixer were examined and grouped into three types such as fast washout, stable signal, and the others as shown in Figure 1b. The first group is connection of “Ef” showed faster washout times (1.3–1.7 s) and moderate signal variations (12–22%). These connections and attitudes for the E-mixer have the same characteristics to the other gas mixers (Figure 1b). The second group is connections “Ec” and “Ed” (manufacturer recommended). These connections represented the best signal variation for a E-mixer (4–6%), but those washout times were 2.0–2.6 s. The second group had similar characteristic to the SH stabilizers (Figure 2). The third group is connections “Ea”, “Ec”, and “Eh”, these connections showed large signal variations and long washout time (Figure 1b). Several connections were possible exception, “Ea3” represents higher stability (7%), and “Eh2” had the fastest washout time (1.1 s) among E-mixers.

**Signal Variation and Washout Time from Stabilizers Coupled with LA-ICPMS.** The T- and Y-mixers are widely employed in the gas lines of LA-ICPMS instruments because of their usability. The signal variation and washout time of “Ya1” showed the best performance among all patterns of each gas mixer (Figure 1a); therefore, we employed the Y-mixer under “Ya1” condition for the evaluations of stabilizers. Almost all stabilizers improved signal variations from 11% (observed for only Ya1-mixer) to 3.0–9.3%, except for the NR stabilizer (13%). The stability of the signal ratio was better than that of the signal intensity in most stabilizers (Table 2). The washout times of all stabilizers with the Y-mixer became longer than those of the only Y-mixer from 1.0 to 1.2–8.9 s as shown in Table 2. The BF stabilizer represented the best stability among all the stabilizers (3.0%), even though it showed the longest washout times (8.9 s). In contrast, the NR stabilizer had worst stability (13%), but the washout time (1.2 s) was similar to that of the Y-mixer. The SH and WR stabilizers showed moderate stabilities (6.6 and 9.3%, respectively) and moderate washout times (2.1 and 1.6 s, respectively).

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**Figure 1.** TRA spectrum of the (a) Y-mixer and (b) E-mixer. Signal intensities are normalized by the top-hat intensity.
DISCUSSION

Reasonable Selection and Effective Utility for a Gas Mixer and a Stabilizer. The E-mixer has fast washout connections (Eb and Ef) and the connections for stable signal (Ec and Ed) as mentioned in previous section. From these results, the E-mixer with connection for a stable signal could be recategorized to be a stabilizer. Among all gas mixers, Y-mixer with “a” connection and no. 1 attitudes is recommended because it represents the fastest washout time (1.0 s) and the smallest signal variation (11%).

The signal variation and the washout time are a conflicting factor for stabilizers as can be seen from Figure 2. The BF stabilizer showed high stability of the signal; however, it had the longest washout time. In contrast, the NR stabilizer showed fast washout but large signal variation. The other stabilizers including the E-mixer showed moderate performance between BF and NR stabilizers as shown in Figure 2.

Here, we suggest an “optimum trade-off line” as indicated in Figure 2 for reasonable selection and effective utility of gas mixers and stabilizers. SH and WR stabilizers and Ed1- and Ya1-mixers were plotted on the trade-off line. In contrast, a gas mixer or a stabilizer, plotted on the upper right area from the “optimum trade-off line”, represents larger signal variation and/or longer washout time. Almost all gas mixers were away from the trade-off line because they had similar washout time (1.0−1.6 s) but unstable signals (>12%). Similarly, AP and BF stabilizers might be away from the trade-off line. Although the signal variation of AP and BF stabilizers (4.6 and 3.0%, respectively) was smaller than those of the Ed1-mixer (4.7%), variation of the signal ratio of the former (4.3 and 5.7%, respectively) was almost the same as those of the Ed1-mixer (4.4%).

A key consideration to select a suitable gas mixer and stabilizer is acceptable washout time with respect to different applications, for example, elemental mapping or bulk analysis, for LA-ICPMS. From Figure 2, a suitable gas mixer or stabilizer on the optimum trade-off line can be selected with respect to different applications.

Table 1. Signal Variation and Washout Time of Gas Mixers

| connection | T-mixer | Y-mixer | N-mixer | C-mixer | E-mixer |
|-----------|---------|---------|---------|---------|---------|
|           | RSD (%) | washout | RSD (%) | washout | RSD (%) | washout | RSD (%) | washout | RSD (%) | washout |
| a1        | 18      | 1.3     | 11      | 1.0     | 22      | 1.6     | 18      | 1.6     | 22      | 2.7     |
| a2        | 18      | 1.3     | 16      | 1.5     | 26      | 1.5     | 24      | 1.1     | 20      | 3.2     |
| a3        | 21      | 1.4     | 15      | 1.2     | 15      | 1.3     | 19      | 1.4     | 7       | 3.2     |
| a4        | 24      | 1.4     | 19      | 1.4     | 19      | 1.3     | 22      | 1.3     | 16      | 5.7     |
| a5        | 15      | 1.3     | 19      | 1.0     | 18      | 1.1     | 32      | 1.5     | 22      | 2.6     |
| average   | 19      | 1.3     | 16      | 1.2     | 20      | 1.4     | 23      | 1.4     | 18      | 3.5     |
| b1        | 13      | 1.3     | 16      | 1.2     | 32      | 1.7     | 12      | 1.4     |
| b2        | 18      | 1.5     | 13      | 1.3     | 12      | 2.7     | 18      | 1.7     |
| b3        | 18      | 1.3     | 20      | 1.4     | 21      | 2.0     | 15      | 1.3     |
| b4        | 17      | 1.3     | 12      | 1.3     | 23      | 1.5     | 14      | 1.4     |
| b5        | 28      | 1.5     | 19      | 1.1     | 28      | 1.4     | 22      | 1.3     |
| average   | 19      | 1.4     | 16      | 1.3     | 23      | 1.9     | 16      | 1.4     |
| c1        | 19      | 1.4     | 21      | 1.2     | 17      | 1.3     | 4.9     | 2.1     |
| c2        | 29      | 1.2     | 15      | 1.5     | 20      | 1.3     | 4.5     | 2.1     |
| c3        | 24      | 1.4     | 18      | 1.5     | 19      | 1.3     | 5.6     | 2.0     |
| c4        | 15      | 1.4     | 17      | 1.4     | 21      | 1.3     | 4.5     | 2.1     |
| c5        | 46      | 1.4     | 18      | 1.2     | 42      | 1.5     | 5.2     | 2.3     |
| average   | 27      | 1.4     | 18      | 1.4     | 24      | 1.3     | 4.9     | 2.1     |
| d1        | 15      | 1.5     | 19      | 1.1     | 25      | 1.8     | 4.7     | 2.6     |
| d2        | 15      | 1.5     | 19      | 1.1     | 32      | 1.6     | 5.9     | 2.3     |
| d3        | 16      | 1.8     | 12      | 1.3     | 16      | 1.8     | 5.0     | 2.3     |
| d4        | 28      | 1.3     | 19      | 1.1     | 28      | 1.3     | 4.8     | 2.4     |
| d5        | 23      | 1.6     | 21      | 1.2     | 23      | 1.6     | 5.0     | 2.3     |
| average   | 33      | 1.4     | 16      | 1.3     | 33      | 1.4     | 16      | 3.3     |
| e1        | 21      | 1.6     | 12      | 1.3     | 21      | 1.6     | 12      | 3.6     |
| e2        | 17      | 1.7     | 21      | 1.4     | 17      | 1.7     | 21      | 2.1     |
| e3        | 11      | 1.7     | 15      | 1.7     | 11      | 1.7     | 15      | 3.2     |
| e4        | 20      | 1.6     | 15      | 1.3     | 20      | 1.6     | 15      | 3.2     |
| e5        | 15      | 1.5     | 18      | 1.4     | 15      | 1.5     | 18      | 2.4     |
| average   | 15      | 1.5     | 18      | 1.4     | 15      | 1.5     | 18      | 2.4     |
| f1        | 16      | 1.3     | 13      | 1.1     | 16      | 1.3     | 13      | 1.1     |
| f2        | 15      | 1.3     | 24      | 2.4     | 15      | 1.3     | 24      | 2.4     |
| f3        | 13      | 1.5     | 19      | 2.5     | 13      | 1.5     | 19      | 2.5     |
| f4        | 13      | 1.4     | 13      | 1.7     | 13      | 1.4     | 13      | 1.7     |
| f5        | 15      | 1.4     | 17      | 2.0     | 15      | 1.4     | 17      | 2.0     |
| average   | 13      | 1.2     | 11      | 1.0     | 15      | 1.1     | 11      | 1.1     | 4.4     | 1.1     |

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different applications. Their best or appropriate signal stability can also be estimated from the optimum trade-off line.

**Effect for Volume of Stabilizers.** Signal stabilities and washout times of Y-mixer, E-mixer, and stabilizers exhibited linear correlation with respect to their volume except for WR stabilizer (Figure 3a,b). The WR stabilizer showed longer washout time and lower stability than those of other stabilizers. This discrepancy could be explained by the internal structure of the WR stabilizer. The BF stabilizer has a couple of division plate to avoid a linear stream of carrier gas. The AP, NR, and SH stabilizers have three or more specific elements, which have a critical role for gas convection. In contrast, a WR stabilizer contained the parallel steel wool, and the linear stream of the carrier gas was not disturbed. The stabilizers except for the WR one have correlations among signal variations, washout times, and their volume. This suggested that the different performances of examined stabilizers were dependent on their volume even though their inner structures were different.

*Particle Filter* Effect. Figure 3c shows averaged signal intensities for gas mixers and stabilizers. The signal intensities from stabilizers were not lower than those without stabilizers. In the past studies, signal intensities with a stabilizer were significantly lower than those without a stabilizer. Therefore, Tunheng and Hirata (2004) noticed that the stabilizers also acted as a particle filter with respect to larger particles. The results in the present study were not corresponded to those of the previous studies.

![Figure 2](http://pubs.acs.org/acsomega/issue/issue.png)

*Figure 2.* Washout time against the stability of signal intensity on the top-hat line. The shaded line represents the optimum trade-off line between signal variation and washout time. The stabilizer on the optimum line is the optimum one for an application.

![Figure 3](http://pubs.acs.org/acsomega/issue/issue.png)

*Figure 3.* Correlation between volume of gas mixers against the (a) washout time, (b) variation of signal intensity, and (c) averaged signal intensity of the top-hat line.

It could be presumed that the reason for no decrease of signal intensity was due to the use of a femtosecond laser. It was recognized that more than 95% of produced particles by lower-fluence (<5 J/cm²) femtosecond laser ablation are smaller than 100 nm. Hence, the signal smoothing effect observed in the present study was ascribed to not only particle filter effect with respect to larger particles but also different phenomena originated from the femtosecond laser with low-fluence operation. In fact, the TRA profiles of LA-ICPMS without any stabilizers represented rare spiky signals (Figure 1). It was plausible that the obtained smooth signal by the low energy femtosecond laser ablation was spatial mixing effect of laser-generated particles in stabilizers.

**CONCLUSIONS**

The analytical efficacy of five gas mixers and five stabilizers was evaluated in the present study. The signal stability of the gas mixers varied greatly because of different connections of the gas lines and different attitudes of the gas mixers. Even in simple gas mixers, the TRA profiles showed large variations, which resulted in a wider range of signal variations. The Y-mixer with a-connection and no. 1 attitude (Ya1) was recommended as the best condition. All stabilizers improved signal stabilities, but washout times became longer than those of the only Y-mixer. Because the signal variation and washout time have a trade-off correlation, stabilizers should be selected reasonably to achieve effective utilization for different applications of LA-ICPMS. Variation of signal stability and washout times using stabilizers correlated with volume despite

**Table 2. Volume, Cross Section, Signal Intensity, Stability, and Washout Time of Stabilizers**

| stabilizer/gas mixer | volume (cm³) | section area (cm²) | top-hat intensity | RSD (int., %) | RSD (ratio, %) | washout time (s) |
|----------------------|--------------|-------------------|-------------------|---------------|----------------|-----------------|
| AP                   | 34           | 3.4               | 26,600            | 4.6           | 4.3            | 4.1             |
| BF                   | 85           | 11                | 26,700            | 3.0           | 5.7            | 8.9             |
| NR                   | 1.6          | 0.14              | 24,800            | 13            | 6.8            | 1.2             |
| SH                   | 22           | 2.2               | 32,500            | 6.6           | 5.2            | 2.1             |
| WR                   | 34           | 3.4               | 30,800            | 9.3           | 10             | 1.6             |
| Ya1-mixer            | 0.1          | 0.03              | 26,800            | 11            | 9.3            | 1.0             |
| Ed1-mixer            | 20           | 2.0               | 26,600            | 4.7           | 4.4            | 2.6             |

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different inner structures. Top-hat intensities were not significant differences through the measurements of a Y-mixer and stabilizers. This suggested that the smoothed signals were not only ascribed to the elimination of larger particle as particle filter effect by a stabilizer. The results obtained and the evaluation in the present study are useful and can be applied to the development of a new gas mixer and stabilizer for LA-ICPMS.

**EXPERIMENTAL SECTION**

**Laser Ablation ICP Mass Spectrometry.** The titanium–sapphire femtosecond laser used in the present study was Cyber IFRIT (Cyber Laser Inc.) equipped with a third harmonic convertor. The wavelength and energy were 260 nm and 30 μJ/cm² fluence, respectively, with a repetition rate of 100 Hz. Galvanometric optics enables an ultrafast scanning (10,000 μm/s) in a sample surface (100×100 μm²) with the laser diameter of ca. 10 μm to achieve stable signals for LA-ICPMS analysis. Analytical sample was set in an in-house sampling cell (T201K in Figure 4), and 800 mL/min of He carrier gas was introduced during LA-ICPMS analysis.

![Figure 4. Schematic diagram of a sampling cell (T201K) used in the present study. The optimal flow rate of He carrier gas was 800 mL/min.](https://dx.doi.org/10.1021/acsomega.0c03658)

The ICP mass spectrometer used in the present study was Agilent 7500cx (Agilent Technologies, Tokyo, Japan), which was quadrupole type of mass spectrometer with the nongas mode. TRA for ICP-MS was applied to obtain time-variable signal intensities of 29Si, 206Pb, and 238U from NIST SRM 610 (trace elements in glass; National Institute of Standards and Technology, Gaithersburg, MD, USA) used as an analytical sample. The dwell time for both 29Si and 238U was 10 ms and that for 206Pb was 20 ms. Consequently, the sweep time of TRA was ca. 50 ms; that is, each data was obtained in a 50 ms cycle. The analytical sequence was controlled by an in-house operating software (galvano laser ablation, OK Lab, Tokyo, Japan). Beginning of data acquisition of ICP-MS, the timing of the laser irradiation and control of the galvanometric laser scanner were triggered by the software. The analytical sequence consisted of 5 s of gas blank, 20 s of laser ablation for NIST SRM 610, and 25 s of signal washout duration. Details of the instrumentation and operational setting are summarized in Table 3.

**Gas Mixer.** Two meters and a half of the Version chemical transfer tubes (SE-200, outside diameter 1/4 in.; inside diameter 1/8 in.) were used as transport tubes between the sampling cell and gas mixer and between the gas mixer and the ICP mass spectrometer, respectively. In the present study, the gas mixing devices for both He gas with laser-generated particles and Ar gas were defined as “gas mixers”. They were also characterized by three gas ports: inlet of He gas with laser-generated particles, inlet of Ar gas, and outlet to ICP-MS.

**Table 3. Instruments and Setting of LA-ICPMS**

| Instrument                  | Monitored Isotope | Scan Mode | Detector | Laser Source | Pulse Duration | Wavelength | Objective Lens | Repetition Rate | Fluence | Galvanometric Driver | Gas Flow | He Carrier Gas | Ar Make-up Gas |
|-----------------------------|-------------------|-----------|----------|-------------|----------------|-------------|----------------|-----------------|---------|---------------------|----------|---------------|---------------|
| 1. ICP mass spectrometer    |                    |           | pulse counting | IFRIT (Cyber Laser, Tokyo, Japan) | 227 fs | 260 nm | f–θ lens (f = 100 mm) with galvanometric optics | 100 Hz | 30 μJ/cm² | Canon GM-1000GC-201 ×2 | 3 gas flow | 800 mL/min | 900 mL/min |

The following five types of gas mixers were evaluated: Swagelok T-union tube fitting (T-mixer; SS-400-3, Swagelok Company; 0.6 cm³), bulb Y-fitting (Y-mixer; VPY-308, ISIS Co., Ltd.; 0.1 cm³), a PEEK nebulizer (N-mixer; Mira Mist nebulizer, Burgener Res. Inc.; <0.1 cm³), a coaxial gas mixer (C-mixer; 8 cm³), and an ESI signal smoothing cell (E-mixer; Elemental Scientific Instruments; 20 cm³).

Connections of three gas lines to three gas ports of each gas mixer were swapped to evaluate the most suitable gas flow directions (a–f of Figure 5). Attitudes of gas mixers (1–5 of Figure 5) were also changed to examine the optimal gas flow directions. Because of the back pressure on off-axis port of the nebulizer (N-mixer), only one direction of connection could be examined (N in Figure 5). Consequently, a total of 95 patterns of the connections and attitudes were examined to compare the signal variation and washout time of gas mixers for LA-ICPMS (Figure 5).

**Stabilizer.** It is not defined commonly the type of device for obtaining a smoothed signal connected to a sample transport tube for LA-ICPMS. The signal stabilizing devices such as a static mixer and a signal smoother used in the present study were defined as “stabilizers”.

The following five stabilizers were examined in the present study: an Apriori static mixer (AP stabilizer; AMX-43X, Apriori Corp.), a Noritake static mixer (NR stabilizer; T3-17, Noritake Co., Ltd.), a Shadis static mixer (SH stabilizer; Y-20A-8E, Younitech Co., Ltd.), a baffled-type stabilizer (BF stabilizer), and a wire-type signal smoother (WR stabilizer; modified after Hu et al., 2012). The WR stabilizer was filled with steel wool (width: 0.7 mm, thickness: 0.1 mm), and the content was 0.13 g/cm³. In the present study, we employed a Y-mixer as a gas mixer for both He and Ar gases to stabilize the ICP between the LA system and these stabilizers.

**Data Processing for TRA Profile.** The TRA profiles were exported in CSV format and processed by spreadsheet software (Excel, Microsoft). Figure 6 shows the TRA profile as an example obtained in the present study. For the TRA profile calculation, the averaged intensity of the gas blank (0–5 and 45–50 s) was subtracted from all signal intensities for each isotope. In order to evaluate the signal variation and washout time of each measurement, the following points were
determined for each TRA profile as shown in Figure 6: a starting point of an up-slope (I), a starting point of a down-slope (II), and washout time (III). The starting point of an up-slope was determined by the beginning of the longest continuous rising of the signal intensities (I in Figure 6).

Because 20 s of the laser ablation was precisely controlled by the software in the LA system, the starting point of a down-slope (II in Figure 6) was defined as exactly 20 s later from the starting point of the up-slope. The washout time (III in Figure 6) was defined as a decay time to the 1% level of signal intensity from the top-hat intensity (99% signal decay). The top-hat line (IV in Figure 6) was set for 10 s after 5 s from the starting point of the up-slope (I). In order to compare each TRA profile, the top-hat line was normalized as 1 as shown in Figure 6. An averaged signal intensity and signal ratio of 206Pb/238U in the top-hat line and their relative standard deviation (RSD, %) were calculated to evaluate the signal stability for both gas mixers and stabilizers.

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Notes

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