Acceleration of Vaporization, Atomization, and Ionization Efficiencies in Inductively Coupled Plasma by Merging Laser-Ablated Particles with Hydrochloric Acid Gas

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To accelerate the vaporization, atomization, and ionization efficiencies in laser ablation inductively coupled plasma mass spectrometry, we merged HCl gas with laser-ablated particles before introduction into the plasma, to convert their surface constituents from oxides to lower-melting chlorides. When particles were merged with HCl gas generated from a HCl solution at 200°C, the measured concentrations of elements in the particles were 135% higher on average than the concentrations in particles merged with ultrapure water vapor. Particle corrosion and surface roughness were observed by scanning electron microscopy, and oxide conversion to chlorides was confirmed by X-ray photoelectron spectroscopy. Under the optimum conditions, the recoveries of measured elements improved by 23% on average, and the recoveries of elements with high-melting oxides (Sr, Zr, and Th) improved by as much as 36%. These results indicate that vaporization, atomization, and ionization in the ICP improved when HCl gas was merged with the ablated particles.

Keywords Laser ablation, NIST glass standard, HCl gas, infrared lamp heating device, conversion from oxides to chlorides, melting points, boiling points, ICP-MS, SEM, XPS

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Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) permits a local, rapid analysis of solid samples. However, incomplete vaporization of ablated particles in the ICP leads to inefficient vaporization, atomization, and ionization.¹ For example, when gold nanoparticles are measured after direct introduction into the ICP, a non-linear calibration curve is observed, owing to incomplete vaporization, and the extent of vaporization decreases with increasing particle diameter.²

We have been monitoring airborne particulate matter (APM) in the Tokyo area since 1995.^{3–5} Recently, Nishiguchi *et al.* realized real-time monitoring by a direct introduction of APM into an ICP by means of a gas exchange device (GED), which permits the exchange of air for argon molecules without the loss of APM.^{6,7} We have reported the use of a GED to determine Pb in a single particle of APM.⁸ However, during real-time monitoring, we found that accurate results could not be obtained for elements that have oxides with high melting points.⁹ Elements in particles introduced into the ICP are measured after melting, vaporization, atomization, and ionization, and the inaccuracies during real-time monitoring have been attributed to incomplete vaporization, atomization, and ionization in the initial radiation zone of the ICP. Günther and co-workers reported that when glass is analyzed by LA-ICPMS, the signal

intensities of elements with high-melting oxides are lower than those of elements with low-melting oxides.^{10,11} Recently, we reported that ablated particles larger than 220 nm could not be decomposed in the ICP when glass is analyzed by LA-ICPMS, and that caused major elemental fractionation.^{12,13}

In this study, we took advantage of the fact that the melting points of the chlorides of elements are lower than those of the corresponding oxides, and we used hydrochloric acid (HCl) gas to convert the oxide constituents of ablated particles to the corresponding chlorides. Specifically, NIST SRM 610, a glass standard, was ablated, and ablated particles with diameters of less than 1 µm were selected by passage through a cascade impactor. Between the impactor and the ICP, we placed an infrared lamp heating device in which HCl gas was merged with the ablated particles, with the goal of improving the vaporization, atomization, and ionization efficiencies of particles introduced into the ICP. The morphology and chemical constituents of the particles after reacting with the HCl gas were investigated by means of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively.

In the ICPMS analyses, ions produced from particles in the ICP were detected by MS, whereas in the SEM and XPS analyses, the particles were measured after being collected on carbon tape. The melting points and boiling points of the elements and their oxides were important parameters that affected the experimental results obtained by ICPMS, SEM, and XPS.

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Fig. 1 Schematic diagram of experimental setup.

Experimental

Instrumentation

A schematic diagram of the experimental setup is shown in Fig. 1. NIST SRM 610, a glass standard, was ablated by means of a LA system (UP213, ESI, Portland, OR, USA) operated in the line-scan mode, and ablated particles in air were collected. An air blank was collected from a class 100 clean bench equipped with HEPA filters. The air blank or ablated particles were introduced into a cascade impactor (inline type with NL-1-1A (<1.0 μm), Tokyo Dylec Co., Tokyo, Japan) at a flow rate of 1.0 L min⁻¹; only ablated particles with diameters of <1.0 μm were measured.

A portion of the sample was introduced at a flow rate of 0.25 L min⁻¹ into a GED (J-Science Lab Co., Kyoto, Japan), which exchanged air for Ar molecules. GED consists of an inner porous glass tube and two outside glass tubes. Ar gas is flowing in the outside gas tubes with a high speed flow rate. There is a pressure difference between inside and outside of the porous glass. Therefore, when a sample is passing through the inner porous glass tube, gas molecules are exchanged from air to Ar, whereas particles remain inside the porous glass. The remaining portion of the sample was vacuumed from the impactor at 0.75 L min⁻¹ by means of a diaphragm pump (FTP-10B, KNF, Tokyo, Japan) equipped with a mass flow controller (MPC0005, Azbil Co., Tokyo, Japan), and ablated particles from this portion of the sample were collected on a cellulose nitrate filter (VSWP04700; pore size, 0.025 μm; Millipore, Tokyo, Japan) over the course of 1 h.

Ablated particles that had passed through the GED were introduced into an infrared lamp heating device by means of a micro diaphragm gas-sampling pump (NMP05L, KNF Neuberger AG, Balterswil, Switzerland). The center of the heating device was a cylindrical glass chamber with a volume of about 190 cm³ (diameter, 20 mm; length, 600 mm), which was designed to mix ablated particles thoroughly with ultrapure water vapor or HCl gas. The diameters of the sample inlets and outlet of a T-shaped joint were 6 mm. The T-shaped inlets consisted of one line for introducing the ablated particles, which came from the LA system through the impactor, and another line for ultrapure water vapor or HCl gas from a mantle heater. The T-shaped outlet was connected to the infrared lamp heating

Table 1 Operating conditions used for LA-ICPMS system

ICPMS model	Agilent 7500ce
RF power	1600 W
Ar carrier gas flow rate	1.05 L min ⁻¹
Make-up Ar gas flow rate	0.45 L min ⁻¹
Sweep Ar gas flow rate	0.60 L min ⁻¹
Ar auxiliary gas flow rate	1.0 L min ⁻¹
Ar plasma gas flow rate	15.0 L min ⁻¹
He gas flow rate in a collision-reaction cell	3.0 mL min ⁻¹
Isotopes measured	⁴⁷ Ti, ⁵⁵ Mn, ⁵⁹ Co, ⁶³ Cu, ⁷⁵ As, ⁸⁸ Sr, ⁹⁰ Zr, ¹⁰³ Mo, ¹⁰⁸ Sn, ¹²¹ Sb, ¹³⁷ Ba, ²⁰⁵ Tl, ²⁰⁸ Pb, ²³² Th, ²³⁸ U
LA model	UP213
Laser type	Nd:YAG
Wavelength	213 nm
Spot size	100 μm
Scan speed	5 μm s ⁻¹
Fluence	2.94 – 5.55 J cm ⁻²
Ablation mode	Line-scan mode
Repetition rate	20 Hz
Carrier gas	Air
Carrier gas flow rate	1.0 L min ⁻¹

device. Three infrared lamps (Heraeus, Hanau, Germany) placed at the outside of the cylindrical glass chamber were controlled by means of a variable transformer (N-130-10, Yamabishi Electric Co., Osaka, Japan). To provide a tight connection between the cylindrical glass chamber and the three lamps, a shield case was designed.

To generate ultrapure water vapor or HCl gas, we used the mantle heater combined with a flask. An ultrapure water or HCl solution was sprayed into the flask by means of a microflow nebulizer (PFA-50, ESI, Omaha, NE, USA) at a carrier gas flow rate of 0.15 L min⁻¹ and a solution flow rate of 50 μL min⁻¹. Vapor introduced into the flask was heated at 200°C, and then the resulting vapor or gas was introduced into the infrared lamp heating device. The air sample or ablated particles and the ultrapure water vapor or HCl gas were merged in the infrared

lamp heating device, and the resulting mixtures were directly introduced into the ICPMS instrument (7500ce, Agilent Technologies, Tokyo, Japan). Heat-resistant Tygon® tubing was used for the pathways through which water vapor and HCl gas flowed. The pathways were covered with a ribbon heater (JK-1, AS ONE Co., Osaka, Japan) kept at 80°C by means of a variable transformer (N-130-10, Yamabishi Electric Co.). The pathways are indicated by shaded lines in Fig. 1. The operating conditions for the LA-ICPMS system are summarized in Table 1.

Reagents

NIST SRM 610 (National Institute of Standards and Technology, Gaithersburg, MD, USA), a glass standard material, was used as a sample. The major forms of the elements in this standard are oxides.¹⁴

A custom multielement standard solution containing Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th, and U (XSTC-384, SPEX CertiPrep Inc., NJ and Ti, Sn, Zr, and Sr standard solutions (1000 ppm, Kanto Chemical Co., Tokyo, Japan) were used as external standards. A Rh standard solution (1000 ppm, Kanto) was used as an internal standard.

Nitric acid (70%, electronic laboratory grade, Kanto), HF (50%, semiconductor grade, Daikin Industries Co., Tokyo, Japan), and H₂O₂ (30%, electronic laboratory grade, Kanto) were used for sample digestion. Diluted HCl (30%, Ultrapure grade, Tama Chemicals Co., Kanagawa, Japan) was used to change the chemical forms of the elements in the ablated particles. Ultrapure water (>18.2 MΩ cm, Milli-Q system, Millipore, Tokyo, Japan) was used to prepare all solutions in this work.

For the sample of X-ray photoelectron spectroscopy (XPS), the NIST SRM 610 glass was ground by an agate mortar, and *t*-BuMe₂SiCl, which was used for a standard of XPS, was laboratory synthesized.

Calibration

A custom multielement standard solution was introduced to the ICPMS *via* an ultrasonic nebulizer coupled with a desolvation system (U6000AT+, CETAC, Omaha, NE) for quantitative analysis (Fig. 1). The sample-introduction efficiency of the nebulizer was constant regardless of the elements, as confirmed in our previous study.⁸ To calculate the sample-introduction efficiency of the ultrasonic nebulizer, we introduced a Cr carbonyl complex standard gas into the ICPMS by means of a metal standard gas generator (J-Science Lab Co.) at a Ar flow rate of 0.05 L min⁻¹. The sample-introduction efficiency of the ultrasonic nebulizer was calculated before each experiment, and was determined to be 2 – 3%.

Optimization of the infrared lamp heating device

The following experiments were carried out to optimize the infrared lamp heating device. First, ablated particles were merged into the infrared lamp heating device along with either ultrapure water vapor or HCl gas generated from 2, 4, and 6 mol L⁻¹ HCl solutions, and introduced *via* the mantle heater/flask combination, and the relative intensities of the measured elements in the various merged solutions were compared. In these experiments, the temperature of the infrared lamp heating device was fixed at 200°C. Second, the relative intensities of the measured elements were compared at temperatures of 200, 300, and 400°C at an HCl concentration of 2 mol L⁻¹.

SEM and XPS observation

The surface of ablated particles, which had been passed through the infrared lamp heating device and collected on a

carbon tape, was analyzed by means of two surface-characterization techniques: SEM (S-4300, Hitachi High-Technologies, Tokyo, Japan) and XPS (AXIS-His 165, Kratos/Shimadzu Co., Kyoto, Japan). Prior to a SEM observation, the surface of the carbon tape was coated with a Pt/Pd alloy by ion sputtering (E-1045, Hitachi High-Technologies). For analysis of the XPS spectrum, Igor software (Ver. 5.0.30, WaveMetrics, Inc., OR, USA) was used.

Calculation of recoveries by comparing direct-monitoring data and filter-collection data

Ablated particles, that were collected on a cellulose nitrate filter (pore size, 0.025 μm) during ICP-MS measurements, were acid-digested as described in the literature.⁴ The recovery (*R*) was calculated by the following equation:

$$R = C_d/C_f \times 100, \% \quad (1)$$

where *C_d* is the element concentration (ng L⁻¹) in ablated particles directly monitored by ICPMS after introduction *via* the infrared lamp heating device, and *C_f* is the element concentration (ng L⁻¹) in filter-collected particles after acid digestion.

In the case of real-time monitoring, ablated particles were directly introduced into the ICP, and ions were measured. In contrast, the elements in the filter-collected particles were measured by ICPMS after acid digestion. 50% HF (3 mL), 70% HNO₃ (6 mL), and 30% H₂O₂ (1 mL) were added to the samples, which were then digested with a microwave digestion system (MLS 1200, Milestone, Italy). After microwave digestion, HF was evaporated by means of a hot plate (230°C). After the solution was reduced to *ca.* 1.0 mL, it was diluted to 10 mL with ultrapure water. Therefore, the elements in the acid-digested particles on the filter were completely ionized in the ICP. Ablated particles, that had been reacted with HCl gas in the infrared lamp heating device, were collected on a filter and digested by the same procedures described above; it was confirmed that there was no loss of ablated particles in the infrared-lamp heating device. Therefore, the vaporization, atomization, and ionization efficiencies of directly introduced ablated particles in the ICP can be evaluated by Eq. (1).

Results and Discussion

Dependence of element increase or decrease ratios on HCl concentration

The melting and boiling points of oxides and chlorides of the elements studied in this work are listed in Table 2.¹⁵ The elements of the NIST SRM 610 glass are present as oxides. We assumed that chlorides were produced by reactions of the ablated particles with the HCl gas.

Ablated particles were merged with ultrapure water vapor or with HCl gas generated from 2, 4, or 6 mol L⁻¹ HCl in the infrared lamp heating device at 200°C. For each element, an increase or decrease ratio was calculated by dividing the signal intensity obtained for ablated particles merged with HCl gas by the signal intensity obtained for ablated particles merged with ultrapure water vapor, and then multiplying the resulting value by 100% (Table 3). The highest ratios were observed when 2 mol L⁻¹ HCl was merged with the ablated particles; under these conditions, the average increase ratio was 132%, whereas the average ratios when particles were merged with 4 and 6 mol L⁻¹ HCl were 114 and 104%, respectively. We suggest that the lower ratios observed when the ablated particles were merged with 4 and 6 mol L⁻¹ HCl were caused by loading

Table 2 Melting and boiling points of oxides and chlorides of elements in NIST SRM 610

Element	Oxide			Chloride		
	Formula	m.p./°C	b.p./°C	Formula	m.p./°C	b.p./°C
As	As ₂ O ₃	274	460	AsCl ₃	-16	130
Tl	Tl ₂ O	579	1080	TlCl	430	720
Sb	Sb ₂ O ₃	655	1425	SbCl ₃	73	220
Mo	MoO ₃	801	1155	MoCl ₂	530 ^a	—
Pb	PbO	897	—	PbCl ₂	501	951
U	U ₃ O ₈	1300 ^a	—	UCl ₄	590	791
Cu	CuO	1446	—	CuCl ₂	630 ^a	—
Sn	SnO ₂	1630	—	SnCl ₂	247	623
Co	CoO	1830	—	CoCl ₂	740	1049
Mn	MnO	1839	—	MnCl ₂	650	1190
Ti	TiO ₂	1843	2900	TiCl ₂	1035	1500
Ba	BaO	1972	—	BaCl ₂	962	1560
Sr	SrO	2531	—	SrCl ₂	874	1250
Zr	ZrO ₂	2709	4300	ZrCl ₂	772 ^a	—
Th	ThO ₂	3390	4400	ThCl ₄	770	921

a. Decompose.

Table 3 Effect of HCl concentration on the increase or decrease ratios at the heating device temperature of 200°C (mean ± SD, *n* = 3)

Element	Ratio, %		
	2 mol L ⁻¹ HCl	4 mol L ⁻¹ HCl	6 mol L ⁻¹ HCl
As	123 ± 27	123 ± 5	147 ± 21
Tl	118 ± 12	110 ± 11	92 ± 7
Sb	128 ± 18	88 ± 6	87 ± 3
Mo	254 ± 45	141 ± 35	124 ± 27
Pb	117 ± 22	112 ± 11	98 ± 10
U	109 ± 17	103 ± 10	85 ± 7
Cu	124 ± 21	125 ± 6	117 ± 9
Sn	168 ± 28	109 ± 8	106 ± 4
Co	129 ± 12	129 ± 15	125 ± 8
Mn	114 ± 15	108 ± 6	101 ± 12
Ti	125 ± 12	122 ± 20	99 ± 8
Ba	121 ± 10	110 ± 13	97 ± 3
Sr	124 ± 16	111 ± 9	100 ± 10
Zr	117 ± 15	114 ± 9	100 ± 8
Th	113 ± 12	99 ± 15	84 ± 3
Average	132	114	104

effects.¹⁶ That is, when a large amount of HCl gas was introduced into the ICP, the energy of the plasma was consumed by vaporization, atomization, and ionization of the HCl gas, and thus the vaporization, atomization, and ionization of the elements was incomplete. Note that arsenic (As) was the only element for which the increase ratio increased with increasing HCl concentration; the ratio was 147% when 6 mol L⁻¹ HCl was introduced. This result was due to interference by ⁴⁰Ar³⁵Cl.

When ablated particles were merged with 2 mol L⁻¹ HCl, the increase ratios were almost the same for all the measured elements, except for Mo. That is, the element-dependence of the effect of HCl on vaporization, atomization, and ionization was low. Our results indicated that the optimum HCl concentration was 2 mol L⁻¹; this concentration was used in subsequent experiments to assess the effect of the heating device temperature on the increase ratios.

Table 4 Effect of the heating device temperature on the increase or decrease ratios at an HCl concentration of 2 mol L⁻¹ (mean ± SD, *n* = 3)

Element	Ratio, %	
	300°C	400°C
As	89 ± 8	159 ± 113
Tl	115 ± 6	160 ± 19
Sb	136 ± 9	171 ± 63
Mo	105 ± 7	90 ± 25
Pb	90 ± 10	58 ± 10
U	120 ± 15	140 ± 10
Cu	117 ± 51	128 ± 10
Sn	120 ± 4	105 ± 9
Co	113 ± 5	127 ± 15
Mn	111 ± 6	119 ± 20
Ti	111 ± 1	137 ± 25
Ba	103 ± 6	119 ± 5
Sr	112 ± 2	128 ± 13
Zr	106 ± 2	125 ± 14
Th	170 ± 62	254 ± 70
Average	115	135

Dependence of increase or decrease ratios on the temperature of the infrared lamp heating device

Ablated particles were merged with 2 mol L⁻¹ HCl in the infrared lamp heating device at 200, 300, or 400°C, and the increase or decrease ratios of the elements were calculated by dividing the element intensities for ablated particles merged with 2 mol L⁻¹ HCl at 300 and 400°C by the corresponding element intensities for particles merged with 2 mol L⁻¹ HCl at 200°C. When ⁵⁹Co, ⁹⁰Zr, and ²³²Th, which have high-melting oxides, were measured, the sampling depth was optimized for each of the three heating device temperatures. The optimum sampling depths at 200, 300, and 400°C were 9.4, 9.1, and 8.9 mm, respectively; that is, optimum sampling depth decreased with increasing heating device temperature, owing to diffusion of ions in the ICP.¹⁷

For all elements, except for Pb and Mo, the increase ratio increased as the heating device temperature was increased (Table 4). The average increase ratios for all the elements were 115 and 135% at 300 and 400°C, respectively. The precisions of Cu and Th were large. Since the precisions of other elements were not so large, the reason for the large precision can be considered to be on artifact after laser ablation or inhomogeneity of the sample surface. We suggest that the increase in temperature promoted HCl-induced conversion of portions of the oxides in the ablated particles to chlorides, corroded the ablated particles, and roughened their surfaces. The variation of the increase ratio with the heating device temperature was correlated with the oxide melting point: at 400°C, large increase ratios were observed for elements with low-melting oxides, such as As, Tl, and Sb (159, 160, and 171%, respectively). We suggest that in the infrared lamp heating device, the extent of melting, atomization, and vaporization of As, Tl, and Sb oxides, which have low melting points and relatively small differences between the oxide and chloride melting points, was higher than that of the high-melting oxides. Therefore, the increase ratios of these low-melting oxides were increased by the heat from the infrared lamp heating device. The increase ratios of U, Cu, Co, Mn, Ti, Ba, Sr, and Zr, which have high-melting oxides (from 1300 to 2709°C), increased only slightly as the heating device temperature was increased. That is,

Fig. 2 SEM images of ablated particles (a) merged with ultrapure water and (b) merged with 2 mol L⁻¹ HCl at the heating device temperature of 400°C.

the temperature dependence of the ratios for these elements was low. We suggest that the effects of corrosion and the change in the chemical form of the surface constituents by reactions with HCl gas were comparable for these elements, and that their vaporization, atomization, and ionization in the plasma were promoted by the increase in the heating device temperature.

In contrast, the increase ratio of thorium (Th) was markedly influenced by the heating device temperature; the ratios for Th at 300 and 400°C were 170 and 254%, respectively. The melting points of Th oxide and Th chloride are 3390 and 770°C, respectively, and the difference between the oxide and chloride melting points is higher for this element than for any of the other measured elements. The change from Th oxide to Th chloride on the particle surface was clearly enhanced by increasing the heating device temperature. The effect of the change in the chemical constituent on the vaporization of ablated particles in the ICP was stronger for Th oxide than for oxides with lower melting points. The ratio for Pb decreased to 58% at the heating device temperature of 400°C. Since the ratio for Pb was improved by using a smaller sampling depth, the reason for this decrease ratio might be caused by the diffusion of ions in front of the sampling cone. In experiments involving the three different temperatures, we achieved the desired acceleration in the vaporization, atomization, and ionization at 400°C. Therefore, we decided that the optimum heating device temperature was 400°C.

SEM observation of ablated particles merged with HCl gas

Figure 2 shows SEM images of ablated particles after they were merged with ultrapure water (Fig. 2a) and 2 mol L⁻¹ HCl (Fig. 2b) in the infrared lamp heating device at 400°C. The surface of the particles merged with water vapor was smooth, whereas the surface of the particles merged with HCl gas was rough. The surface was corroded by 2 mol L⁻¹ HCl, the surface area of the particles increased, and the surface became friable. As a result, particles merged with 2 mol L⁻¹ HCl received more energy from the ICP than those merged with ultrapure water, and vaporization, atomization, and ionization of the particles merged with HCl gas were accelerated in the ICP. As shown in Table 3, the increase in the increase ratio was not element dependent when ablated particles were merged with ultrapure water or with 2 mol L⁻¹ HCl at a heating device temperature of 200°C. Surface corrosion was a major reason for the increase in the increase ratios at the heating device temperature of 200°C.

XPS observation of ablated particles merged with ultrapure water vapor or HCl gas

Ablated particles were collected on three different carbon tapes after merging with ultrapure water and 2 mol L⁻¹ HCl in the infrared lamp heating device at 400°C, and XPS spectra were measured ($n = 3$). Since similar results were obtained,

Fig. 3 Silicon 2p XPS spectra. (a) Ablated particles merged with ultrapure water at the heating device temperature of 400°C: XPS spectrum (open circles), peak fit (black line), and SiO₂ (blue line). (b) Ablated particles merged with 2 mol L⁻¹ HCl at the heating device temperature of 400°C: XPS spectrum (open circles), peak fit (black line), SiO₂ (SiO₂ + Na₂O, blue line), SiCl₂ (SiO₂ + Na₂O, red line). (c) Mixture (1:1) of NIST SRM 610 powder and 97% *t*-BuMe₂SiCl: XPS spectrum (open circles), peak fit (black line), SiO₂ (SiO₂ + Na₂O + *t*-BuMe₂SiCl, blue line), SiCl₂ (SiO₂ + Na₂O + *t*-BuMe₂SiCl, green line).

one result is shown in this paper. Figure 3a shows the Si 2p XPS spectrum of ablated particles collected on a carbon tape after

merging with ultrapure water. When the peak indicated by the black line was mathematically separated by means of Igor software, the single peak (peak top, 102.7 eV) indicated by the blue line was obtained. The NIST XPS database¹⁸ indicates that the SiO₂ peak occurs between 103.0 and 104.0 eV, but the SiO₂ peak observed in this study was shifted to lower energy. The SiO₂ peak is shifted to low energy when glass consisting of a mixture of SiO₂ and Na₂O is measured by XPS, and the energy of the SiO₂ peak is 0.8 eV lower than that of the SiO₂ crystal when the proportions of SiO₂ and Na₂O are 69 and 31%, respectively.¹⁹ The position of the peak shown by the blue line in Fig. 3a was in a good agreement with the XPS peak for a mixture of SiO₂ and Na₂O. Therefore, we assigned the peak at 102.7 eV to SiO₂.

Figure 3b shows the Si 2p XPS spectrum of ablated particles collected on a carbon tape after merging with 2 mol L⁻¹ HCl. The red and blue lines were obtained by the peak separation of the XPS spectrum, indicated by the black line. The peak indicated by the blue line was assigned to SiO₂. The top of the peak indicated by the red line was -1.0 eV from the top of the peak indicated by the blue line. The energy difference between the XPS peak of SiO₂ with Na₂O and the peak of SiCl₂ is 1.0 eV.¹⁸ The energy difference of the red line was in good agreement with the energy difference of SiCl₂. The chemical shift of SiCl₂ was observed when ablated particles were merged with 2 mol L⁻¹ HCl at 400°C. We assumed that the constituents of the particles were partially converted to chlorides when the particles were merged with 2 mol L⁻¹ HCl in the infrared lamp heating device at 400°C. The area ratio of the SiO₂ and SiCl₂ peaks in Fig. 3b was 1/0.24.

We ground NIST SRM 610, which contains 72% SiO₂, in an agate mortar; and we mixed the resulting powder in a 1:1 weight ratio with 97% *t*-BuMe₂SiCl (which contains Si-Cl bonds) and measured the XPS spectrum of the mixture (Fig. 3c). The peaks indicated by the blue and green lines were obtained by the peak separation of the spectrum shown by the black line. The peak indicated by the blue line originated from SiO₂, and that indicated by the green line (peak top, 101.0 eV) was assigned to SiCl₂. The ratio of the SiO₂ and SiCl₂ peak areas was 1/0.66. To estimate the proportion of SiO₂ that was changed to SiCl₂, we calculated the SiO₂ and SiCl₂ ratio in particles merged with 2 mol L⁻¹ HCl at 400°C from the SiO₂/SiCl₂ peak area ratio in Fig. 3c. When the SiO₂/SiCl₂ ratio was 1:1, the SiO₂/SiCl₂ peak area ratio was 1/0.66 (Fig. 3c); whereas the SiO₂/SiCl₂ ratio in ablated particles merged with HCl gas was 1/0.24 (Fig. 3b). Therefore, the SiO₂/SiCl₂ ratio when particles were merged with 2 mol L⁻¹ HCl at 400°C was 1/0.36, where 0.36 was calculated by dividing 0.24 by 0.66. The ratio of chlorides to the total constituents can be calculated as $0.36/(1.00 + 0.36) = 0.26$. This result indicates that 26% of Si oxides were changed to chlorides on the surface. However, the XPS spectra were measured only to a depth of about 10 nm on the surface of the particles, which had diameters of less than 1 μm. It is likely that the constituents in the core of the ablated particles were not changed.

Recovery under optimum conditions

We determined the element recovery ratios under the optimum conditions (2 mol L⁻¹ HCl, 400°C) at a sampling depth of 8.9 mm (Fig. 4). The recoveries of all the elements, except for As, were higher when ablated particles were merged with 2 mol L⁻¹ HCl than when they were merged with ultrapure water. The average increase in the recovery for the measured elements was 23%. The recoveries of elements with high-melting oxides increased substantially; *e.g.*, the recoveries of Sr, Zr, and Th increased from 66 to 95%, from 67 to 99%, and from

Fig. 4 Recovery ratios as a function of the oxide melting point, obtained by merging ablated particles with 2 mol L⁻¹ HCl at the heating device temperature of 400°C and a sampling depth of 8.9 mm. Experiments we repeated three times ($n = 3$).

32 to 68%, respectively. For high-melting oxides, vaporization, atomization, and ionization in the ICP were accelerated by merging the ablated particles with 2 mol L⁻¹ HCl in the infrared lamp heating device at 400°C. Note that because polyatomic ⁴⁰Ar³⁵Cl interferes with ⁷⁵As, masses of 77 and 78 were simultaneously measured, and the recovery of ⁷⁵As was determined by means of the interference correction equation²⁰ (Fig. 4 shows the recovery of As after interference correction). Ablated particles collected on a filter were microwave-digested, and then a hot plate was used for the evaporation of hydrofluoric acid. There is a possibility that volatile elements, such as As and Sb, were not completely collected on a filter, or might have been partially vaporized during acid digestion on a hot plate. For that reason, the concentration of Sb in filter-collection data was low and the recovery of Sb became 130%. The recoveries of Mo, Pb, and U were relatively low: 71, 35, and 63%, respectively, when the particles were merged with HCl gas. The melting points of the oxides of Mo, Pb, and U are 801, 897, and 1300°C, respectively. Because the vaporization, atomization, and ionization of these elements in the ICP were accelerated by merging of the particles with HCl gas in the infrared lamp heating device, the ions diffused in front of the sampling cone, which decreased the recovery of elements with low-melting oxides. In contrast, the recoveries of As, Ti, Mn, Ba, Sr, and Zr were 100 ± 10%.

To eliminate the diffusion of ions of elements with low-melting oxides, we changed the sampling depth from 8.9 to 8.4 mm, and then determined the element recoveries under the optimized conditions (Fig. 5). Under these conditions, the recoveries of Mo, Pb, and U improved from 71 to 123%, from 35 to 81%, and from 63 to 112%, respectively, when the particles were merged with HCl gas. This improvement likely resulted from more-efficient sampling of the ions produced from the ablated particles. However, changing the sampling depth decreased the recoveries of elements with high-melting oxides; specifically, the recoveries of Mn, Ti, Ba, Sr, Zr, and Th decreased by about 45% relative to the recoveries at a sampling depth of 8.9 mm. This change was caused by the short plasma residence time. In the ablated particles, high-melting oxides were incompletely vaporized, atomized, and ionized in the ICP, and therefore the recovery decreased.

Fig. 5 Recovery ratios as a function of the oxide melting point, obtained by merging ablated particles with 2 mol L⁻¹ HCl at the heating device temperature of 400°C and a sampling depth of 8.4 mm. Experiments we repeated three times ($n = 3$).

Conclusions

Merging ablated particles with HCl gas produced by heating an HCl solution resulted in an average 135% increase in the element concentrations compared with concentrations obtained when the particles were merged with ultrapure water. The increase could be explained by two factors: a change in the chemical constituents of the particles from oxides to chlorides and a change in the surface roughness and friability of the particles. XPS results indicated that 26% of Si oxides were changed to Si chlorides on the surface of ablated particles merged with 2 mol L⁻¹ HCl at the heating device temperature of 400°C. The increase ratio of the elements increased as the temperature of the infrared lamp heating device was increased. On average, the increase ratio increased by 135% when the temperature of the infrared lamp heating device was increased from 200 to 400°C. The change in the increase ratio was dependent on the oxide melting point. The increase ratios for As, Tl, and Sb, which have relatively low-melting oxides and relatively small differences between the oxide and chloride melting points, were increased less by the increase of the infrared lamp heating device temperature than was the increase ratio for Th, which has a high-melting oxide and a large difference in the melting point between the oxide and chloride, and which showed a remarkable increase when the heating device temperature was increased. The chemical change in the particle constituents was promoted by the increase in the heating device temperature; this promotion resulted in an increase in the increase ratio.

When ablated particles were merged with 2 mol L⁻¹ HCl at heating device temperature of 400°C, the element recovery at a sampling depth of 8.9 mm increased by 23% on average relative to the recovery when ablated particles were merged with ultrapure water. The recoveries of Sr, Zr, and Th, which have high-melting oxides, were 29, 32, and 36% higher, respectively, than the recoveries with ultrapure water. The recoveries of elements with relatively low-melting oxides, such as Mo, Pb, and U, decreased when particles were merged with 2 mol L⁻¹ HCl, owing to the diffusion of ions prior to the sampling cone. Changing the sampling depth from 8.9 to 8.4 mm improved the recoveries of Mo, Pb, and U from 71 to 123%, from 35 to 81%, and from 63 to 112%, respectively, when the particles were

merged with HCl gas. This improvement likely resulted from more-efficient sampling of the ions produced from the ablated particles. This experimental result suggests that special attention to the diffusion of ions is necessary when elements with relatively low-melting oxides are measured.

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