Quantitative Analysis of Trace Elements in Silicate Glass Sample by LA-ICP-QMS/QMS with an ORC: Silicon as the Matrix of Calibrating Solutions and the Internal Standard for Measurement

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A strategy was presented for quantitative analysis of trace elements in a glass sample by laser ablation inductively coupled plasma tandem quadrupole mass spectrometry (LA-ICP-QMS/QMS) with an octapole reaction cell (ORC). Silicon in the glass was used as the internal standard as well as the matrix for making the calibrating solutions. Sample aerosols generated by the laser ablation system were introduced into the dual pass spray chamber through the make-up gas port. Calibrating solutions were nebulized into the spray chamber using a microflow nebulizer. The silicon matrix-matched calibrating solutions produced a calibration curve capable for the quantitative analysis of trace elements in a silicate glass sample, NIST SRM 612. The analytical results agreed with the certified values, taking into consideration their expanded uncertainties. The detection limits for Cr, Mn, Fe, Ni, Cu, As, Sr, Ag, Cd, Sb, Ba, and Pb, were respectively 0.3, 0.08, 0.5, 0.4, 0.19, 1.1, 0.1, 0.02, 0.03, 0.025, 0.09, and 0.07 μg g⁻¹.

Keywords LA-ICP-QMS/QMS, quantitative analysis, trace element, matrix, internal standard

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Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) allows for direct analysis of the elements in a solid sample without dissolution of the sample, but the calibration strategy is often challenging for quantification analysis by LA-ICP-MS. Various calibration strategies for LA-ICP-MS have been reported and applied to the analysis of geological, environmental, biological, and medicine samples. However, there is not a single calibration strategy covering all kinds of samples. Therefore, improvement of calibration strategies for LA-ICP-MS is still required for quantitative analysis.

In most research, matrix-matched standards were required for quantitating purpose, based on external calibration, response coefficient factor, or sum-normalization approach. In recent years, in order to overcome the limitation of the availability of solid calibration standards, “solid-liquid” calibration strategies, i.e., standard solutions for calibration, were studied for the quantitative analysis by LA-ICP-MS. Such kinds of strategies have been successfully applied to the analysis of steel, glass, apple leaves, polyethylene material, chemical standards, alloy, and biological samples. Calibration curve strategy and standard addition have been proposed for quantitative analysis by LA-ICP-MS, both of which required that the stability of sample quantity transported into the plasma. However, the stability of the laser power and the physical homogeneity of the sample may result in the variation of sample quantity ablated, affecting the accuracy of the measurement.

Glass is a popular target of LA-ICP-MS because a lot of kinds of solid samples could be prepared in homogenous glass samples by alkali fusion. Silicon is one of the major components in silicate glass samples and is a potential internal standard element for quantitative analysis of a glass sample. However, attention should be paid to spectral interferences for the analysis of silicon isotopes, because the stable isotopes of silicon, 28Si⁺, 29Si⁺, and 30Si⁺ suffer spectral interferences from ¹⁴N₂⁺, ¹⁴N₂¹H⁺ (and ¹⁴N¹⁵N⁺), and ¹⁴N¹⁶O⁺, respectively. In recent years, tandem quadrupole ICP-MS (i.e., ICP-QMS/QMS) with an octapole reaction cell (ORC) system has become available, which permits the highly sensitive analysis of silicon isotopes by effective separation of spectral interferences.

In the present work, a calibration strategy is proposed for the quantitative analysis of trace elements in a glass sample by LA-ICP-MS with an ORC system, while the calibration was carried out using standard solutions with silicon matrix. A standard solution was introduced into the spray chamber using a micro-flow nebulizer, while the sample aerosol generated by the LA system was introduced into the chamber through the make-up gas port of the chamber. The solution mist and the sample aerosol were mixed in the chamber and introduced into the plasma. Instead of matrix-matched solid standards often reported, matrix-matched solution standards were prepared and used for quantitation in the present experiment. Moreover, instead of transferring the standard solution mists to dried aerosols, the sample aerosols were transferred to wet condition by continuously introducing a blank solution during the analysis of the sample. The set-up of the present measurement system does not...
not require any additional devices (for example, desolvation device or even T-connector) except for the initial LA system and the ICP-QMS/QMS.

To the best knowledge of the author, there have been few reports on the metrological application of LA-ICP-MS techniques up to now, which could be partly attributed to the difficulty of ensuring the traceability of the measurement, especially the sample mass transported into the ICP-MS. In the present experiment, the concentration of Si in the sample was determined precisely and used as the internal standard (indicating the sample mass) as well as the matrix for making the calibration standards. The traceability of the measurement was ensured through metrological traceable standard solutions of Si and trace elements. Uncertainty of the measurement could be evaluated by taking into consideration the standard uncertainty of each parameter.

Experimental

Instrumentation

An ICP-QMS/QMS system (Agilent 8800, Agilent Technologies Japan, Tokyo, Japan) with an ORC system was applied for the measurement of the elements. The typical operating conditions are summarized in Table 1, in which the parameters were optimized daily to obtain the best sensitivity for analysis. Measurements of the elements were carried out with MS/MS mode and all the elements were measured on mass, i.e. the m/z of the first QMS was identical to that of the second QMS. Based on a preliminary optimization, the present experiment was carried out using NH3 gas as the reaction gas to achieve the highest signal to blank ratio.

As the default parts, there are a make-up gas port on the end-cap of the spray chamber and an optional gas port on the high matrix introduction (HMI) connector of the Agilent 8800 ICP-QMS/QMS. The structure of the spray chamber and the HMI connector to the torch is illustrated in Fig. 1. Both the make-up gas port and optional gas port could be used to introduce the sample aerosols generated by the LA system.

An LA system (NWR213, Electro Scientific Industries, Inc. Japan, Tokyo, Japan) was applied in the present experiment. The LA system was equipped with a (100 × 100 mm) high performance TwoVol ablation chamber. High purity helium gas was used as the chamber gas for the LA system and controlled by the built-in mass flow controller. The typical operating conditions for the LA system in the present experiments were as follows (unless noted otherwise): laser frequency, 10 Hz; sample surface energy, 10 J cm⁻²; laser spot diameter, 100 μm; scanning speed, 10 μm s⁻¹; carrier gas, He 0.90 mL min⁻¹. All the measurements were carried out at line scanning.

Chemicals and materials

In order to ensure the metrological traceability of the results, single element standard solutions (1000 mg L⁻¹, guaranteed by the Japan Calibration Service System, JCSS) of Ag, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Si, and Sr were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Furthermore, preparation of the calibrating solutions was carried out using an electronic balance calibrated by JCSS. Ultrapur® grade HNO3 for making standard solutions was also purchased from Kanto Chemical Co., Inc. Pure water used throughout the present experiment was prepared using a Millipore purification system (Elix, Nihon Millipore Kogyo, Tokyo, Japan).

Scheme for calibration

In the present work, the concentrations of trace elements in silicate glass were determined by LA-ICP-QMS/QMS with calibration curves based on Si-concentration matched standard solutions. The scheme for calibration is illustrated in Fig. 2. At first, the concentration of Si in the sample was determined by LA-ICP-QMS/QMS using standard solutions of Na, Ca, and...
Al with Si. Secondly, the concentrations of trace elements were determined by LA-ICP-QMS/QMS using standard solutions of trace elements with Si as the matrix and the internal standard, where the concentration of Si determined in the first step was used to calculate the concentrations of trace elements.

Calculation for calibration of Si

A preliminary qualitative measurement was carried out for the present glass sample, i.e., NIST SRM 612. The results confirmed that the major elements of the sample were Si, Na, Ca, and Al. The sample was a compound of the oxides of these elements, forming the natural chemical property of silicate glass. Considering the fact that the concentrations of other elements were extremely low, the sum of the concentrations of these oxides is 1 as shown in Eq. (1), where M was the element Si, Na, Ca, and Al.

$$\Sigma [M_{xO_y}] = 1 \quad (1)$$

In Eq. (1), $[M_{xO_y}]$ was the concentration (unit, g g$^{-1}$) of the oxide $M_{xO_y}$, while $x$ and $y$ were the numbers of $M$ and $O$ atoms in one molecule of the oxide.

In the present work, $[M_{xO_y}]$ was measured by the measurement of $[M]$. Therefore, Eq. (1) could be transformed to Eq. (2).

$$\Sigma \left( \frac{[M]}{[M_{xO_y}]} \right) = 1 \quad (2)$$

When both sides of Eq. (2) were divided by $[Si]$, Eq. (3) could be obtained.

$$\Sigma \left( \frac{[M]}{[Si]} \frac{[M_{xO_y}]}{[M]} \right) = \frac{1}{[Si]} \quad (3)$$

After transformation of Eq. (3), $[Si]$ could be calculated based on Eq. (4).

$$[Si] = \frac{1}{\Sigma \left( \frac{[M]}{[Si]} \frac{[M_{xO_y}]}{[M]} \right)} \quad (4)$$

Based on the atomic weight of each element, the $\frac{[M_{xO_y}]}{[M]}$ for Si, Na, Ca, and Al was 2.139, 1.348, 1.399, and 1.889, respectively.

When the $\frac{[M]}{[Si]}$ was determined, the $[Si]$ could be calculated.

It is noted that the total concentrations of Na$_2$O, CaO, Al$_2$O$_3$, and SiO$_2$ account for 99% of the present sample so that the concentration of Si could be calculated from the ratios to Na, Ca, and Al. For an unknown sample, major contents of the elements should be determined in advance. The ratios to other elements were the numbers of $M$ and $O$ atoms in one molecule of the oxide.

Calculation for calibration of other elements

In the linearity range of the ICP-MS measurement, the relationships between the elemental concentration and the signal intensity could be expressed with Eqs. (5) - (8).

$$S^M = [M] \times a^M + b^M \quad (5)$$

$$S^M = [M] \times a^M + b^M \quad (6)$$

$$S^Si = [Si] \times a^{Si} + b^{Si} \quad (7)$$

After transformation, the concentration of element $M$ could be calculated based on Eq. (12).

| Parameter | Meaning | Unit |
|-----------|---------|------|
| $S^M$ | Signal intensity of element $M$ in the solution | CPS |
| $[M]$ | Concentration of element $M$ in the solution | μg g$^{-1}$ |
| $a^M$ | Slope of the calibration curve for element $M$ in the solution | — |
| $b^M$ | Intercept of the calibration curve for element $M$ in the solution | — |
| $S^Si$ | Signal intensity of Si in the solution | — |
| $[Si]$ | Concentration of Si in the solution | μg g$^{-1}$ |
| $a^{Si}$ | Slope of the calibration curve for Si in the solution | — |
| $b^{Si}$ | Intercept of the calibration curve for Si in the solution | — |
Results and Discussion

Improvement of measurement precision by mixing the sample aerosols with the solution mist in the spray chamber

A preliminary optimization of the carrier gas (Ar) for the nebulizer and the LA chamber gas (He) was carried out to obtain the highest elemental signal intensity by introducing the tuning solution containing 1 ng g⁻¹ of Co, Y, Ce, and Tl each in 0.3 mol L⁻¹ HNO₃. The results indicate that the best nebulizer efficiency was achieved with the carrier gas at 0.9 L min⁻¹. Furthermore, the highest elemental signal intensities were achieved with the chamber gas at 0.9 L min⁻¹. Therefore, all of the following experiments were carried out with the carrier gas at 0.9 L min⁻¹ for the nebulizer and the chamber gas at 0.9 L min⁻¹ for the LA system.

In the present work, elemental standard solutions were used to make the calibration curve. In order to obtain better measurement precision, a comparison was carried out by using the make-up gas port and optional gas port for introducing sample aerosols. A standard solution of 1.0 ng g⁻¹ Co in 0.3 mol L⁻¹ of HNO₃ was nebulized into the spray chamber during the comparison test, while sample aerosols were provided by ablating NIST SRM 612 wafer.

\[ [M]_{\text{opt}} = \frac{S_{\text{opt}}}{S_{\text{m}}} \times \frac{S_{\text{m}}}{S_{\text{opt}}} \times [M]_{\text{sub}} \]

(12)

\[ \text{RSU} = \frac{\text{signal intensity}}{\text{CPS}} \]

Fig. 3 Analytical results of Si (in sample aerosol) and Co (in solution mist) using the make-up gas port and optional gas port for introduction of the sample aerosols (laser spot size, 10 μm). (a) Signal intensity of \(^{28}\text{Si}^+\), (b) signal intensity of \(^{59}\text{Co}^+\). ---, Option gas port; —, make-up gas port.

Fig. 4 The results of Si signal intensity dependence on sample surface energy.

The results are plotted in Figs. 3(a) and 3(b), where the plots shown in solid lines and dotted lines were respectively obtained by using the make-up gas port and the optional gas port for the introduction of sample aerosols. As can be seen in Fig. 3(a), the signal intensities of \(^{28}\text{Si}^+\) (aerosol of solid sample from the LA system) obtained with the optional gas port for sample aerosol introduction were higher than those obtained with the make-up gas port. By contrast, as can be seen in Fig. 3(b), the signal intensities of \(^{59}\text{Co}^+\) (mist of standard solution from the nebulizer) obtained with the optional gas port for sample aerosol introduction were lower than those obtained with the make-up gas port. These results could be attributed to the following facts. When the optional gas port was used for the introduction of sample aerosols, the introduction of solution mist (Co standard) into the torch was partly suppressed (so-called dilution effect applied for high matrix samples). When the make-up gas port was used for the introduction of sample aerosols, the introduction of solution mist into the torch was improved while the sample aerosols were diluted by the increase of solution mist.

It is notable that, the relative standard uncertainties (RSUs) of the \(^{59}\text{Co}^+\) measurement shown in Fig. 3(b) were almost identical to each other, where the standard uncertainty was calculated by dividing the standard deviation by the square root of the number of measurement. It indicates that the highly precise measurement of the solution mist contents was not dependent on the gas port for sample aerosol introduction. However, as is shown in Fig. 3(a), despite the relative high signal intensity, the RSU of \(^{28}\text{Si}^+\) measurement obtained with the optional gas port for particle introduction was worse than that obtained with the make-up gas port. These results might indicate that the spray chamber acted as a stabilizer of the particles and got rid of spiking larger particles; such phenomenon has been reported as "damping effect".\(^{24}\)

In order to improve the precision of measurement, the sample aerosols were introduced with the make-up gas port in the following experiment.

Optimization of laser power

The NWR-213 LA system was operated at specified fluence in the present work. In order to find the optimum fluence, dependence of the \(^{28}\text{Si}^+\) signal intensity on the laser power was investigated in the sample surface energy (SSE) range of 0 to 12.5 J cm⁻² fluence.
The results are plotted in Fig. 4. As can be seen, the signal intensity of 28Si+ increased gradually with the increase of laser power in the SSE range from 0 to approximately 10 J cm−2 fluence. These results indicate that the increase of laser power resulted in more sample ablated and transferred to the ICP-QMS/QMS system. However, when the SSE exceeded 10 J cm−2 fluence, further increase of laser power did not result in the increase of sample quantity for analysis. Therefore, the operation of the LA system was fixed to achieve SSE of 10 J cm−2 fluence in the following experiment.

Dependence of the measurement precision on ablating frequency

The present NWR-213 ablation system could be operated at 1, 2, 4, 5, 10, and 20 Hz. Dependence of the measurement precision on the frequency of the LA system was investigated to find an optimum operating condition.

The results of selected elements are plotted in Figs. 5(a) and 5(b), for the signal intensity and the RSU respectively. As can be seen from Fig. 5(a), the signal intensity of each element is in proportion to the frequency of the LA system, i.e., a higher frequency resulted in a higher signal intensity. By contrast, as can be seen from Fig. 5(b), the measurement precision was improved (with lower RSU) by increasing the frequency. In general, when the frequency was under 5 Hz, the RSU was over 1%, which might indicate that there were not enough samples ablated for continuous measurement by ICP-QMS/QMS. On the other hand, the measurement precision was not apparently improved at 20 Hz in comparison to that obtained at 10 Hz. Therefore, the LA system was operated at 10 Hz in the following experiment.

Matrix effect of Si on the measurement of trace elements

Si is the major element of silicate glass as the natural property. It is required to check the matrix effect of Si for the accurate measurement of trace elements in silicate glass.

A series of standard solutions in 0.3 mol L−1 HNO3 with various Si concentrations was prepared and analyzed to check the matrix effect of Si. The concentrations of Si in the standard solutions were 0, 1, 5, 10, 15, 20, 25, and 50 μg g−1, respectively. The concentration of each target element was 10 ng g−1 in the standard solutions.

The results of relative signal intensity were plotted in Fig. 6, where the relative signal intensity was calculated as the ratio of the signal intensity in a standard solution to that in the standard solution without Si, i.e., 0 μg g−1 of Si. As can be seen from Fig. 6, the relative signal intensities in the standard solutions with various concentrations of Si were generally lower than 1.00, i.e., which indicates that the signal intensities of the elements were suppressed by Si to some extent. This indicates that matrix-matched standard solutions were required for precise analysis of the element. It also can be seen that the suppression extent of the signal intensities generally increased with the increase of Si concentration. However, the relative signal intensities of each element obtained with Si concentration of 15, 20, and 25 μg g−1 were close to one another, indicating that the standards made in 20 μg g−1 of Si might be useful for the analysis of the elements in a standard solution with 15 to 25 μg g−1 of Si. This fact indicates that the concentration of Si in the standard solutions was not extremely critical for the quantitation analysis by LA-ICP-MS, i.e., closely matrix-matched standard solutions are acceptable for quantitation purposes. This is an important issue for the present method; it permitted the accurate quantitation of the elements with slight fluctuations of the quantity of the ablated sample.

A preliminary test was carried out to check the quantity of Si experiment.

It is noted that the results of Ni, Mn, and Sr were representatively plotted in Fig. 5, while similar results were also obtained for other elements measured in the present experiment.

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A preliminary test was carried out to check the quantity of Si
obtained by introduction of 0.3 mol L–1 of HNO3 (using the equivalent concentration (BEC). The LLDs and BECs were determined. The results of Cr, Mn, Fe, Ni, Cu, As, Sr, Ag, Cd, Sb, Ba, and Pb are summarized in Table 3, along with the certified values, lower limit of detection (LLD), and blank uncertainty of measurement with a coverage factor (k) = 2.

Table 3 Analytical results of trace elements in NIST SRM 612

| Element | Concentration/(μg g⁻¹) | Certified value | Observed value | LLD | BEC |
|---------|-------------------------|-----------------|----------------|-----|-----|
| Cr      | 35 ± 3.3                | 34.2 ± 1.7      | 0.3            | 4.0 |
| Mn      | 37.7 ± 3.8              | 38.1 ± 1.2      | 0.08           | 0.19|
| Fe      | 51 ± 2                  | 51.7 ± 1.4      | 0.5            | 5.2 |
| Ni      | 38.8 ± 0.2              | 38.4 ± 1.6      | 0.4            | 0.7 |
| Cu      | 37.7 ± 0.9e             | 45.3 ± 1.7      | 0.19           | 0.8 |
| As      | 37.4 ± 2.2              | 42.0 ± 4.3      | 1.1            | 2.8 |
| Sr      | 78.4 ± 0.2              | 75.2 ± 3.8      | 0.10           | 0.4 |
| Ag      | 22 ± 0.3                | 26.6 ± 1.8      | 0.020          | 0.024|
| Cd      | 29.9 ± 4.2              | 28.1 ± 2.5      | 0.030          | 0.007|
| Sb      | 34.9 ± 2.2              | 40.4 ± 2.0      | 0.025          | 0.009|
| Ba      | 38.6 ± 2.6              | 37.0 ± 1.5      | 0.09           | 0.09|
| Pb      | 38.57 ± 0.2             | 44.8 ± 3.1      | 0.07           | 0.08|

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| Cr      | 35 ± 3.3                | 34.2 ± 1.7      | 0.3            | 4.0 |
| Mn      | 37.7 ± 3.8              | 38.1 ± 1.2      | 0.08           | 0.19|
| Fe      | 51 ± 2                  | 51.7 ± 1.4      | 0.5            | 5.2 |
| Ni      | 38.8 ± 0.2              | 38.4 ± 1.6      | 0.4            | 0.7 |
| Cu      | 37.7 ± 0.9e             | 45.3 ± 1.7      | 0.19           | 0.8 |
| As      | 37.4 ± 2.2              | 42.0 ± 4.3      | 1.1            | 2.8 |
| Sr      | 78.4 ± 0.2              | 75.2 ± 3.8      | 0.10           | 0.4 |
| Ag      | 22 ± 0.3                | 26.6 ± 1.8      | 0.020          | 0.024|
| Cd      | 29.9 ± 4.2              | 28.1 ± 2.5      | 0.030          | 0.007|
| Sb      | 34.9 ± 2.2              | 40.4 ± 2.0      | 0.025          | 0.009|
| Ba      | 38.6 ± 2.6              | 37.0 ± 1.5      | 0.09           | 0.09|
| Pb      | 38.57 ± 0.2             | 44.8 ± 3.1      | 0.07           | 0.08|

Fig. 7 Calibration curve and analytical results for the determination of the concentration of Na in the sample. \( S_{\text{cal}} \) and \( S_{\text{ns}} \), signal intensity of Na and Si, unit CPS; [Na] and [Si], concentration of Na and Si, unit ng g⁻¹.

Measurement of the concentration of Si in NIST SRM 612

According to the certificate of NIST SRM 612, the major compounds are SiO₂ (72%), Na₂O (14%), CaO (12%), and Al₂O₃ (2%). Because Si was used as the internal standard for calibrating trace elements, the concentration of Si was determined in the present experiment.

Based on calibration curves made from standard solutions with 20.0 μg g⁻¹ of Si and different concentrations of Na, Ca, and Al, their [M]/[Si] ratios were observed to be (0.313 ± 0.004), (0.252 ± 0.006), and (0.0318 ± 0.0002), respectively. The number following the “±” symbol was the expanded uncertainty of measurement with a coverage factor (k = 2). As a result, the concentrations of Si and SiO₂ were (0.336 ± 0.006), (0.252 ± 0.004), and (0.0318 ± 0.0002) μg g⁻¹ in the sample. The calibration curve for the measurement of [Na]/[Si] is representatively plotted in Fig. 7.

Results of trace elements in NIST SRM 612 obtained with the present method

Based on the above-mentioned calibration method, the concentrations of trace elements in NIST SRM 612 were determined. The results of Cr, Mn, Fe, Ni, Cu, As, Sr, Ag, Cd, Sb, Ba, and Pb are summarized in Table 3, along with the certified values, lower limit of detection (LLD), and blank equivalent concentration (BEC). The LLDs and BECs were obtained by introduction of 0.3 mol L⁻¹ of HNO₃ (using the nebulizer) without ablation of the sample. The LLD was the concentration corresponding to 3σ of the BEC. As summarized in Table 3, the LLDs and BECs were low enough for the determination of the elemental concentrations. The expanded uncertainty of the observed values in Table 3 were calculated with a coverage factor (k = 2) corresponding to 95% of confidential interval. It can be seen that the expanded uncertainties of the observed values were generally comparable to those of the certified values.

The observed values shown in bold fonts, i.e., for Cr, Mn, Fe, Ni, As, Sr, Cd, and Ba, indicate that these results agreed with the certified values, taking into consideration the expanded uncertainties of both values. On the other hand, the observed values of Cu, Ag, Sb, and Pb were comparable to but slightly higher than the certified values (or reference value), even taking into consideration the expanded uncertainty of both values. Taking into consideration the fact that the melting points of the elements were relatively lower, such relatively higher values might be partly attributed to the possible fractionation during the ablation process even though a relatively mild laser power was applied in the present experiment. In any case, these results were covered by the ranges of reported concentrations of Cu, Ag, Sb, and Pb in NIST SRM 612.

The results obtained with the present method are generally in agreement with the certified values, indicating that the present method is valid for the measurement of trace elements in a silicate glass sample. Because the concentration of Si (as the matrix and the internal standard) in the sample could also be determined in the present method, it can be applied to unknown samples.

The accuracy and the precision of the present work were comparable to or better than those in other reports on the determination of elements in NIST SRM 612. It is notable that some elements were not determined in those reports, e.g., As, Ag, Cd, Cu, and Sb, which might be attributed to the lack of proper calibration standards. By contrast, all of these elements could be determined based on liquid standards solutions as suggested in the present work.

Uncertainty of the measurement

The uncertainty of the measurement of each element given in Table 3 was evaluated considering the uncertainty of each parameter in Eq. (12). The typical value and the standard uncertainty of each parameter in Eq. (12) for the measurement of Mn is representatively summarized in Table 4, along with the contribution to the combined uncertainty (u.c.). It is noted that [M]ₜₐ is given in Table 4 as well as the parameters in Eq. (12). The typical value of [M]ₜₐ is 0 since the calculation based on Eq. (12) was carried after blank correction. The standard uncertainty of [M]ₜₐ was calculated as the concentration.
Table 4  Budgets for the measurement of Mn

| Parameter | Typical value | Standard uncertainty | Unit | Contribution, % |
|-----------|---------------|----------------------|------|-----------------|
| S\textsuperscript{i0} | 1.01 x 10\textsuperscript{6} | 4.71 x 10\textsuperscript{4} | CPS | 8.1 |
| [M]\textsubscript{i} | 7.25 x 10\textsuperscript{-3} | 2.54 x 10\textsuperscript{-5} | µg g\textsuperscript{-1} | 4.6 |
| S\textsuperscript{i} | 2.96 x 10\textsuperscript{7} | 8.53 x 10\textsuperscript{6} | CPS | 3.1 |
| [Si]\textsubscript{i} | 2.00 x 10\textsuperscript{-6} | 7.00 x 10\textsuperscript{-6} | g g\textsuperscript{-1} | 4.5 |
| S\textsuperscript{i}\textsubscript{i} | 3.66 x 10\textsuperscript{6} | 3.99 x 10\textsuperscript{5} | CPS | 44.3 |
| S\textsuperscript{i}\textsubscript{2} | 3.47 x 10\textsuperscript{7} | 3.38 x 10\textsuperscript{6} | CPS | 34.6 |
| [Si]\textsubscript{2} | 3.36 x 10\textsuperscript{-1} | 5.00 x 10\textsuperscript{-1} | g g\textsuperscript{-1} | 0.8 |
| [M]\textsubscript{blank} | 0.00 | 8.00 x 10\textsuperscript{-3} | µg g\textsuperscript{-1} | <0.1 |
| [M] | 37.7 | | µg g\textsuperscript{-1} | |

\(\mu\) value unit Contribution, \% 

Consideration of the uncertainty of each parameter used for the measurement. It can be seen that the major contributions to the combined uncertainty were from the measurement of S\textsuperscript{i0} and S\textsuperscript{i}, 44.3% and 34.6%, respectively. The expanded uncertainty for the measurement of Mn with the coverage factor of \(k = 2\) was 1.2 µg g\textsuperscript{-1}, approximately 3%.

Conclusions

Simultaneous introduction of sample aerosols generated by the LA and the solution mist generated by the nebulizer was carried out using the dual pass spray chamber. After accurate determination, Si could be used as the internal standard as well as the matrix for the standard solution. The analytical results of NIST SRM 610 indicate that Si-matched standard solutions based calibration curves are valid for the measurement of trace elements in silicate glass by LA-ICP-QMS/QMS. The traceability of the results was ensured by using metrological traceable elemental standard solutions, along with the solution preparation using the calibrated electronic balance. The uncertainty of the measurement could be evaluated by taking into consideration the uncertainty of each parameter used for the calibration.

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