Multiple channels Concentric Grid Nebulizer for Online Standard Addition in Inductively Coupled Plasma Optical Emission Spectrometry

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ABSTRACT

A multiple channel type concentric grid nebulizer (m-CGrid) was developed for realizing an efficient online standard addition in inductively coupled plasma optical emission spectrometer (ICP-OES) without pre-mixing of liquids before nebulization. The m-CGrid can nebulize two independent liquids without premixing due to a unique structure, having two independent liquid-flow capillaries inside a single nozzle and a grid screen (over 350 mesh per inch) being put on the hole of the nozzle. The grid acts as both a flow damper and sieve; two liquids are well-mixed with a gas flow in a small space just before the grid screen, and the mixture breaks-up into small droplets by passing through the grid. The m-CGrid nebulizer provides almost the same or better spray performance compared with a conventional nebulizer such as Meinhard nebulizer; the primary aerosols were much finer ($D_{50}$: 2.9 µm and 3.1 µm for two channels) than those generated with Meinhard nebulizer type C ($D_{50}$: 19.5 µm). The signal intensities in ICP-OES obtained with two liquid channels were almost the same and were two-to four-fold higher than that obtained with the Meinhard nebulizer for 23 elements. The performances of m-CGrid in an online standard addition were demonstrated in the analysis of NIST SRM1577b bovine liver and NIES No.3 Chlorella. The analytical results were in good agreement with their certified values.

Keywords: multiple-channels, nebulizer, grid, standard addition, ICP-OES
INTRODUCTION

Inductively coupled plasma optical emission spectrometry (ICP-OES) is widely used for elemental analysis in various research fields\textsuperscript{1,2}. A nebulizer is one of the important parts for improving analytical performances of ICP-OES, especially in the analysis of high matrix samples. Key performance indexes of nebulizer are a fineness of primary aerosols and a tolerance for matrices.\textsuperscript{3} A fine aerosol generation is beneficial to increase signal intensities in ICP-OES due to the increase in the loading amount of aerosols into the plasma. A high tolerance for matrices such as total dissolved solids (TDS) allows the analysis of problematic samples such as salts rich solutions routinely analyzed by ICP-OES. Therefore, many nebulizers have been developed for improving an efficiency of aerosol generation and/or high TDS tolerance, launching various nebulizers on a market.\textsuperscript{3}

With spreading applications of ICP-OES, an interest for simultaneous nebulization of multiple liquids has been increasing for realizing an efficient on-line standard addition for compensation of matrix effects.\textsuperscript{3} Matrix effects are major technical issues to be care in ICP-OES, and a standard addition method is a robust way to compensate the effects.\textsuperscript{1,2} However classical standard addition method is time and labor consuming, because individual calibration curves for each sample should be made, requiring preparation and measurement of numerous solutions.

One way to overcome the above drawback is making an online standard addition system. Online standard addition with a T-pipe mixing has been investigated,\textsuperscript{4-6} and alternative systems using a multi-nebulizing unit has been developed for improving an efficiency of an online standard addition.\textsuperscript{7-17} Several multi-nebulizing systems have
been developed using (i) two nebulizers with one or two spray chamber,$^{7-10}$ (ii) multiple-nozzle nebulizer,$^{11-14}$ (iii) cross-flow nebulizer having multiple liquid channels.$^{15-17}$

Above all systems can simultaneously introduce sample and standard solutions into the plasma without pre-mixing, but have other drawbacks for sensitivity, reproducibility, and/or handling.

The drawbacks of type (i) and (ii) systems are coarse aerosol generations and difficulty in synchronizing the performances of individual sprays. Aerosols generated with the type (i) and (ii) systems would be coarser compared with a system using single nebulizer with a single nozzle, because the total gas flow for sample introductions have to be split to two nebulizers or nozzles for controlling the residence time of aerosols inside the plasma. In addition, each nebulizer or nozzle independently works, resulting in the variances of the loading amounts of two liquids into the plasma. High performance nebulizers such as high efficiency nebulizer (HEN),$^9$ flow blurring nebulizer (FBN),$^{10}$ and multi-spray type FBN,$^{11-14}$ which can generate finer aerosols than conventional nebulizers, was applied to improve the performance of the type (i) and (ii) systems. Even though each spray performance with a low gas flow rate was competitive to conventional concentric nebulizers with high gas flow rate, the sprays in these systems would not synchronize, which was potentially large variance source of analytical results.

The type (iii) systems have a structural advantage against the other types, no need to split a gas flow due to a single nozzle structure, which is promising for overcoming the above drawbacks of type (i) and (ii). The cross-flow nebulizers in type (iii) have two or three liquid channels that make a cross-point at an exit of a gas flow. These can simultaneously spray two or three liquids, with a single gas flow exit, thereby no need to split the gas flow to each channel. However, aerosols generated with typical cross-flow
nebulizers are coarser than the case of conventional concentric nebulizers, mostly due to less effective gas-liquid contact compared with concentric type nebulizers. In addition, the end-points of each channel strongly influence spray performances, but it is hard to precisely adjust the position, resulting in a significant difference of spray performances of channels.\textsuperscript{16}

For overcoming the drawback of the type (iii) systems, we evolved a concentric type grid nebulizer (CGrid)\textsuperscript{18} to a multiple-channel type nebulizer (m-CGrid), then applied to online standard addition. The m-CGrid can simultaneously spray two independent liquids without premixing, maintaining excellent spray characteristics of the original CGrid such as fineness of aerosols and tolerance for TDS. These are due to a unique structure, having two independent liquid-flow capillaries inside a single nozzle and a grid screen (over 350 mesh per inch) being put on the hole of the nozzle. The grid acts as both a flow damper and sieve, thereby two liquids are well-mixed with a gas flow inside the nozzle, in a small space just before the grid screen, then break-up into small droplets by passing through the grid. In this paper, we evaluate the spray performance of the m-CGrid nebulizer through the comparison with that of a Meinhard nebulizer, and demonstrate its applicability to an online standard addition/ICP-OES by analyzing certified reference materials, NIST SRM1577b bovine liver and NIES No.3 Chrorella.

**EXPERIMENTAL**

*Multiple-channels Grid Nebulizer (m-CGrid)*

A schematic diagram of m-CGrid is shown in Fig. 1. The structure of m-CGrid was almost the same as the original CGrid, consisting of a laboratory made PEEK body
(i.d./o.d.: 0.5 mm/6.0 mm), two capillaries (i.d./o.d.: 150 µm/220 µm), PEEK grid screen (356 mesh), and nozzle end cap (nozzle hole i.d.: 200 µm). The two capillaries were fixed with 1/16 FEP sleeves and 1/16 PEEK fittings with an adhesive material. Both capillary tips were set at a position recessed by ca. 20-100 µm from the grid screen.

**Instrumentation**

The ICP-OES used was a Perkin-Elmer Optima 7300 DV. The operating conditions are summarized in Table 1, almost the same as described in ref.18. Two types of nebulizers, Meinhard nebulizer type C (MHN: TR-50-C1, Meinhard, US) and the original CGrid (AIF-05, S.T. Japan, Japan) were used for comparing their analytical performances with that of m-CGrid. All the nebulizers were attached to a baffled cyclone spray chamber, and liquids were introduced by using a liquid chromatography pump (LC-10Ai, Shimadzu, Japan) with an automatic injection valve (VA-11, FLOM, Japan). The nebulizer gas flow rates were set to obtain the highest value of the ratio Mg(II) 280.269 nm/Mg(I) 285.213 nm; from 0.55 L min⁻¹ to 0.60 L min⁻¹ for m-CGrid and the original CGrid, and from 0.60 L min⁻¹ to 0.65 L min⁻¹ for MHN.

For evaluating the analytical performance of nebulizers coupled to ICP-OES, several atomic and ionic lines covering a wide range of energy sum values ($E_{\text{sum}}$: sum of excitation energy ($E_{\text{exc}}$) and ionization energy ($E_{\text{ion}}$)) were measured. The emission lines measured were listed in Table 2.

**Reagents**

Working standard solutions in HNO₃ (2 % wt/wt) were prepared from either a multielement standard solution containing twenty-three elements (ICP Multielement
standard solution IV CertiPUR, Merck, Darmstadt, Germany) or single element standard solutions (1000 mg L\(^{-1}\) each, Kanto Chemical Industries, Ltd., Japan). Concentrate nitric acid used was Ultrapur® 100 (70 %, Kanto Chemical, Japan). Pure water prepared by a Milli-Q water purification system (resistivity 18 M\(\Omega\) cm, Merck, Japan) was used throughout the experiments.

The reference materials used for validation of the online standard addition were NIST standard reference material bovine liver SRM 1577b (National Institute of Standards and Technology, NIST, US) and NIES No.3 Chlorella (National Institute of Environmental Studies, NIES, Japan)

**Size measurement of primary aerosols**

The size distribution of the primary aerosols was measured by using a laser diffraction system (LDS, Aerotrac LDSA-SPR1500A, Nikkiso Co., Japan). The laser focus distance was 100 mm, and the measurement range of an aerosol diameter was 0.5 \(\mu\text{m}\) to 355 \(\mu\text{m}\). The measurement position was 5 mm from the nebulizer tip through the centerline of the spray cone. A nebulized liquid was Milli-Q water, which was introduced at 0.50 mL min\(^{-1}\) by using LC-10Ai. The nebulizer gas flow rates were set at 0.6 L min\(^{-1}\) for all the nebulizers.

**Online standard addition**

The setup of the sample introduction unit for online standard addition is summarized in Fig. 2. Two sets of the LC pumps (LC-10Ai) and the automatic injection valves (VA-11) were connected to individual liquid channels of m-CGrid by using a 1/16 PEEK tube (i.d. 0.25 mm) and 1/16 PEEK fittings, as is summarized in Fig. 2. Carrier
solutions of both channels were 2% nitric acid solutions, and the volumes of the injection loops were 3.0 mL for sample solutions and 1.0 mL for standard solutions.

The measurement procedure was consisting four steps, displayed in Fig. 3. In this system setup, ca. 20 s was required to obtain a steady-state signal after injecting solutions. Therefore, 30 seconds intervals were inserted between the steps. A detail of the procedure is as follows: step 1: carrier solutions (2% nitric acid solutions) were introduced into both the channels. Step 2: 3 mL of a sample solution was introduced into the channel A via the injection valve. The signals were measured after 30 s for obtaining the steady-state signal. Step 3 & 4: 1 mL of standard solutions (STD1 and 2) having different concentrations of target elements were sequentially introduced into the channel B with 60 s intervals. The signals were measured after 30 s from each injection. The injection loops were washed with a 2% nitric acid solution during the interval. Liquid flow rates of the channels were slightly different in several percent, which might originate from an instrumental bias of the LC pumps. For correcting the difference of the flow rate, an internal standard correction was adopted, where Ytterbium was selected as the internal standard element and spiked in both sample and standard solutions. The measurement time for each sample was only 6 min, consisting of 4.5 min for online standard measurement and 1.5 min for washing of the liquid flow lines.

**Digestion of reference materials**

Both NIST SRM 1577b and NIES No.3 were digested with a pressurized microwave digestion system (UltraWAVE, Milestone General, Italy), where three sub-samples for both CRM were digested all at once. The digestion procedure was as follows. Approximately 0.5 g of the sub-sample was weighted into digestion vessels, then
5 mL of HNO₃ was added into the vessels. The vessels were set into the clave of the UltraWA VE, and N₂ gas was purged by 40 psi. The digestion temperature and time were set at 290 deg and 40 min, respectively. The digests were diluted with Milli-Q water up to ca. 50 mL. A procedure blank solution was prepared in the same manner.

RESULTS AND DISCUSSION

Evaluation of the spray performance

The spray performance of m-CGrid was evaluated based on the diameters of the primary aerosols. Fig. 4 (a) shows the size distributions of primary aerosols generated by m-CGrid for two liquid channels, where liquid was introduced to one channel and the other one was plugged. The liquid flow rate was set at 0.5 mL min⁻¹ and the nebulizer gas flow rate was set at 0.60 L min⁻¹. The size distributions of primary aerosols generated by the original CGrid having single liquid channel and MHN are also shown in Fig. 4 (b) as references, where the liquid flow rates were set at 1.0 mL min⁻¹ and the nebulizer gas flow rate was set at 0.60 L min⁻¹.

It is clearly seen in Fig. 4 (a) and (b), the distribution patterns for two liquid channels of m-CGrid were quite similar, and the primary aerosols were much finer than those by MHN, almost the same as that of the original CGrid. The diameters below which 50 % of aerosol by volume is contained (D₅₀) were: Channel A: 2.9 μm, Channel B: 3.1 μm, original CGrid: 2.8 μm, MHN: 19.5 μm. They indicate that the spray performances of two channels are almost the same, and that the fineness of primary aerosols does not worsen by adding the second liquid channel inside the nozzle.

The m-CGrid has quite unique features compared with other multiple spray
nebulizers. Kovachev et. al. reported the spray performance of multi-spray type flow focusing nebulizer, having multiple nozzles. The spray performances of the nozzles were quite different; Sauter mean diameters, $D_{3,2}$ for individual nozzles were from $12 \mu m$ to $17.5 \mu m$. The value of $D_{3,2}$ is usually almost the same or smaller than the value of $D_{50}$, and the $D_{3,2}$ values of the multiple nozzles were much larger than the $D_{50}$ value obtained with a single nozzle type flow focusing nebulizer ($D_{50}: 3.82 \mu m$). In addition, the sprays of each nozzle would not synchronize, requiring further corrections for channel dependent variances. Bauer et. al. demonstrated the performance of multi-spray type cross flow nebulizer with two liquid channels. The sprays of two liquid channels would synchronize due to a single nozzle, but it would be difficult to achieve the same spray performances for two liquid channels. This is due to the difficulty in setting the tips of the channel capillary, which is a drawback for manufacturing. Indeed, the signal intensities in ICP-OES obtained with individual channels (shown in ref. 16) were significantly different, reflecting a difference of the spray performances, though the size distributions of primary aerosols generated by individual channels were not reported. One the contrary, the sprays of two liquid channels of m-CGrid are well synchronized, and no special cares for setting the tips position. These are great advantages for online standard addition.

A tolerance for total dissolved solid (TDS) and an effect of a viscosity of spraying liquid are important factors for evaluating the performance of nebulizers. The m-CGrid could continuously spray a saturated NaCl solution during 5 hours without no clogging inside the nozzle, indicating the same TDS tolerance of the original CGrid. Physical properties such as surface tension and viscosity significantly influence on the spray performance of pneumatic type nebulizers, and the trends of the influences would not be
different between MHN and m-CGrid.\textsuperscript{3,20,21} Except for mixing hydrophilic organic solvents having a lower surface tension, a surface tension of aquatic solutions would not be dramatically changed, expecting less influence in spraying performance. On the other hands, a viscosity of a spraying liquid significantly changed, typically when sulfuric acid, highly viscous liquid is mixed, might changing a spray performance.

For estimating the effect of viscosity on spraying performance of m-CGrid, mixtures of elemental standard solutions (Mg, Cr, Co, Cu, Zn, Fe, and Y) with and without 5\% H\textsubscript{2}SO\textsubscript{4} were measured by ICP-OES equipped with m-CGrid and MHN, then the ratios of the signal intensities with and without 5\% H\textsubscript{2}SO\textsubscript{4} were compared. In this measurement, the total liquid flow rates (signal channel was used for m-CGrid) were set at 1.0 mL min\textsuperscript{-1} and the nebulizer gas flow rate was set at 0.60 L min\textsuperscript{-1}. Signal channel was used for m-CGrid. The results were summarized in Fig.6. For both nebulizers, all the signal intensities decrease 2\% to 12\% with 5\% H\textsubscript{2}SO\textsubscript{4}, and no significant differences in the levels of the decreases were observed, even though the loading amount of aerosols into the plasma by using m-CGrid was much larger than the case of MHN. Although 5\% H\textsubscript{2}SO\textsubscript{4} not only increases a viscosity but also induces chemical interferences inside the plasma, the above results might indicate that the contribution of a viscosity on the spray performance of m-CGrid are smaller than that for MHN.

**Evaluation of the performance in ICP-OES**

The performance of m-CGrid in ICP-OES was evaluated by measuring standard solution. Fig. 5 showed the comparison of signal intensities obtained by using channel A and B, expressed as the ratio of the signal intensities. In this comparison, 2\% HNO\textsubscript{3} solution was continuously flowed in both channels, and standard solution was introduced
to channel A and B in turns using the injection valve. It is clearly seen that the almost the same signal intensities for all the elements were obtained by using both channels.

The ratios of signal intensities obtained with the channel A of m-CGrid to those obtained with the MHN were summarized in Fig. 7, where the liquid flow rates were set at 1.0 mL min\(^{-1}\) (0.5 mL min\(^{-1}\) for each channel) for m-CGrid, and 1.0 mL min\(^{-1}\) for MHN. The nebulizer gas flow rates were optimized for obtaining maximum signal intensities by using each nebulizer. The signal intensities obtained with m-CGrid showed the similar trend as the case using the original CGrid;\(^{18}\) that is, 2- to 3-fold higher signal intensities for all the measured lines were obtained compared with those with MHN. The increase of the signal intensities was mostly due to a fineness of primary aerosols, thereby increased the total amount of tertiary aerosols passed through the spray chamber. In addition, the magnification of the increase of the signal intensities was correlated with the energy sum \(E_{sum}\) values, which might depend on the difference of the plasma robustness by using m-CGrid and MHN. Indeed, the robustness index value of the plasma (Mg(II) 280.269 nm/Mg(I) 285.213 nm) by using m-CGrid (11.1) was much better than that for MHN (9.2),\(^{18}\) mostly due to increase in electron density by increasing the loading amount of water vapor into the plasma.\(^{22-25}\) These results indicate that the performance of the channels in ICP-OES are almost the same, providing much higher signal intensities with a high robustness for concomitant matrix in ICP-OES compared with MHN.

An influence of the ratio of liquid flow rates of both channels was evaluated, because a dilution factor of a sample solution in the spray can be reduced by decreasing only the flow rate of standard solution, obtaining higher signal intensities for a sample solution. Figure 8 shows the dependence of a signal intensity on the ratio of liquid flow rates of sample and standard solutions. In the evaluation, Cu standard solution (0.5 mg kg\(^{-1}\) with
2 % HNO₃) was introduced into the channel A, and 2 % HNO₃ solution was introduced into the channel B. The sum of liquid flow rate of two channels was fixed at 1 mL min⁻¹, while the ratio of the liquid flow rates of the channels was varied. It is clearly seen that the Cu signal intensity increased with increase of the flow rate, and linearly increased in the range of 0.4 mL min⁻¹ to 0.9 mL min⁻¹. Below 0.4 mL min⁻¹, the relation between the liquid flow rate and signal intensity was not linear, more decreasing with the decrease of the flow rate. This was mostly due to a difference of a pressure of the liquid flow, because the tubes having the same inner diameter and length were used for the channels. However, the decrease does not significantly influence on an analytical reliability obtained by the present online standard addition method, because it can be easily correct by the internal standard correction. In addition, a stable signal could be obtained when the flow rate of the standard solution was significantly lower than the flow rate of the sample solution, depending on the stability of a pumping flow rate. Indeed, the relative standard deviation of Cu signal at the flow rate of 0.05 mL min⁻¹ (+ 0.95 mL⁻¹ of 2 % HNO₃ solution) in this experiment was less than 3 % (n = 10).

**Multi-elemental analyses of CRMs by online standard addition**

Two CRMs, NIST SRM 1577b Bovine Liver and NIES CRM No.3 Chlorella, were analyzed to validate the online standard addition method using m-CGrid. The analytical results obtained are summarized in Table 3, where the observed values are expressed as mean values and their expanded uncertainties (n = 3, coverage factor k = 2). The mean values were calculated from three measurement data (one measurement for each subsample). The expanded uncertainties were evaluated in accordance with the *Guide to the Expression of Uncertainty in Measurement* (GUM:1995). Both analytical results
were in good agreement with the certified and reference values within their uncertainties, indicating the performance of m-CGrid is well suited for realizing online standard addition method in ICP-OES.

CONCLUSION

A multiple channels CGrid was developed for realizing an efficient online standard addition in ICP-OES. The m-CGrid can nebulize two independent liquids with an excellent spray performance, mostly due to the unique structure; the primary aerosols generated were much finer than those for MHN, resulting in 2- to 3-fold higher signal intensities in ICP-OES with a good stability. In addition, the spray performances for two liquid channels are almost the same. Even though a correction of the difference of liquid flow rates of the channels originated from an instrumental bias of the LC pumps was required, it can be easily done with applying the internal standard correction. The performances of m-CGrid in an online standard addition were demonstrated by analyzing NIST SRM1577b bovine liver and NIES No.3 Chrorella. All the analytical results were in good agreement with their certified and reference values. These results indicate that m-CGrid is well suited for online standard addition in ICP-OES.

ACKNOWLEDGEMENT

The authors express sincere appreciation to S.T. Japan INC. and Mr. Masaaki Abe for supporting the present research.
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Table 1  Operating conditions of the ICP-OES.

| Parameter                  | Value                      |
|---------------------------|----------------------------|
| Incident Rf power         | 1.4 kW                     |
| Frequency                 | 40 MHz                     |
| Outer gas flow rate       | 15 L min⁻¹                 |
| Intermediate gas flow rate| 0.2 L min⁻¹                |
| Sheath gas                | Nitrogen 0.3 L min⁻¹       |
| Torch injector            | Alumina (i.d. 2.0 mm)      |
| Spray chamber             | Twister cyclone chamber (baffled) |
| Nebulizer gas flow rate   | 0.55 L min⁻¹ - 0.60 L min⁻¹ for m-CGrid and original CGrid |
|                          | 0.60 L min⁻¹ - 0.65 L min⁻¹ for MHN |
| Liquid flow rate          | 0.5 mL min⁻¹ for each channel of m-CGrid |
|                          | 1 mL min⁻¹ for MHN         |
| Integration & read time   | 1 s                        |
| View mode                 | Axial                      |

Table 2  Energy values for the emission lines.

| Emission type | Element | Wavelength / nm | $E_{\text{ion}}$ / eV | $E_{\text{exc}}$ / eV | $E_{\text{sum}}$ / eV |
|---------------|---------|-----------------|------------------------|------------------------|------------------------|
| Atomic line   | Cr I    | 357.87          | 3.5                    | 3.5                    | 3.5                    |
|               | Cu I    | 327.39          | 3.8                    | 3.8                    | 3.8                    |
|               | Mg I    | 285.21          | 4.4                    | 4.4                    | 4.4                    |
|               | Mn I    | 279.48          | 4.4                    | 4.4                    | 4.4                    |
|               | Ni I    | 232.00          | 5.4                    | 5.4                    | 5.4                    |
|               | Cd I    | 228.80          | 5.4                    | 5.4                    | 5.4                    |
|               | Pb I    | 217.00          | 5.7                    | 5.7                    | 5.7                    |
|               | Zn I    | 213.86          | 5.8                    | 5.8                    | 5.8                    |
| Ionic line    | Cr II   | 267.72          | 6.8                    | 4.6                    | 11.4                   |
|               | Mg II   | 280.27          | 7.7                    | 4.5                    | 12.1                   |
|               | Mn II   | 257.61          | 7.9                    | 4.4                    | 12.3                   |
|               | Ni II   | 231.60          | 7.6                    | 5.4                    | 13.0                   |
|               | Pb II   | 220.35          | 7.4                    | 5.6                    | 13.0                   |
|               | Fe II   | 238.20          | 7.9                    | 5.2                    | 13.1                   |
|               | Cu II   | 224.70          | 7.7                    | 5.6                    | 13.3                   |
|               | Cd II   | 214.44          | 9.0                    | 5.8                    | 14.8                   |
|               | Zn II   | 206.20          | 9.4                    | 6.0                    | 15.4                   |
Table 3 Analytical results for each CRMs obtained by on-line standard addition ICP-OES with m-CGrid.

| Element | NIST SRM 1577b Bovine Liver | NIES CRM No.3 Chlorella |
|---------|----------------------------|-------------------------|
|         | Observed value\(^1\) | Certified value\(^2\) | Observed value\(^3\) | Certified value\(^2\) |
| P       | 11200 ± 300 mg kg\(^{-1}\) | 11000 ± 300 mg kg\(^{-1}\) | 17000 ± 800 mg kg\(^{-1}\) | 17000\(^3\) mg kg\(^{-1}\) |
| K       | 10200 ± 600 mg kg\(^{-1}\) | 9940 ± 20 mg kg\(^{-1}\) | 12900 ± 300 mg kg\(^{-1}\) | 12400 ± 600 mg kg\(^{-1}\) |
| Na      | 2230 ± 110 mg kg\(^{-1}\) | 2420 ± 60 mg kg\(^{-1}\) | N/A\(^4\) | N/A |
| Mg      | 593 ± 12 mg kg\(^{-1}\) | 601 ± 28 mg kg\(^{-1}\) | 3290 ± 40 mg kg\(^{-1}\) | 3300 ± 200 mg kg\(^{-1}\) |
| Fe      | 185 ± 9 mg kg\(^{-1}\) | 184 ± 15 mg kg\(^{-1}\) | 1880 ± 70 mg kg\(^{-1}\) | 1850 ± 100 mg kg\(^{-1}\) |
| Cu      | 159 ± 9 mg kg\(^{-1}\) | 160 ± 8 mg kg\(^{-1}\) | 3.4 ± 0.4 mg kg\(^{-1}\) | 3.5 ± 0.3 mg kg\(^{-1}\) |
| Zn      | 128 ± 2 mg kg\(^{-1}\) | 127 ± 16 mg kg\(^{-1}\) | 20.9 ± 0.7 mg kg\(^{-1}\) | 20.5 ± 1.0 mg kg\(^{-1}\) |
| Ca      | 118 ± 7 mg kg\(^{-1}\) | 116 ± 4 mg kg\(^{-1}\) | 4910 ± 50 mg kg\(^{-1}\) | 4900 ± 300 mg kg\(^{-1}\) |
| Mn      | 10.6 ± 0.3 mg kg\(^{-1}\) | 10.5 ± 1.7 mg kg\(^{-1}\) | 71 ± 6 mg kg\(^{-1}\) | 69 ± 5 mg kg\(^{-1}\) |
| Sr      | N/A | N/A | 39.7 ± 1.3 mg kg\(^{-1}\) | 40 ± 3 mg kg\(^{-1}\) |

\(^1\) mean ± expanded uncertainty (coverage factor \(k = 2\), calculated from the results of three sub-samples.

\(^2\) typical value ± expanded uncertainty (coverage factor \(k = 2\)

\(^3\) Reference Values

\(^4\) Not applicable
FIGURE CAPTIONS

Fig. 1 Schematic image of m-CGrid.

Fig. 2 Setup of the sample introduction unit for online standard addition

Fig. 3 Schematic image of the online standard addition procedure based on typical measurement profile

Fig. 4 Size distributions of primary aerosols generated by (a) individual two liquid channels of m-CGrid, (b) the original CGrid and MHN: liquid flow rate $Q_l = 0.5 \text{ mL min}^{-1}$ for two channels of m-CGrid, and $1.0 \text{ mL min}^{-1}$ for the original CGrid and MHN; gas flow rate $Q_g = 0.60 \text{ L min}^{-1}$ for all the nebulizers.

Fig. 5 Comparison of signal intensities obtained by using channel A and B, where 2% HNO$_3$ solution continuously flowed in both channels and a standard solution was introduced into the channel A and B in terns.

Fig. 6 Ratios of signal intensities in ICP-OES with and without 5 % H$_2$SO$_4$ by using m-CGrid (white-bar) and MHN (black-bar).

Fig. 7 Comparison of signal intensities obtained by using m-CGrid and MHN.
Fig. 8  Dependence of signal intensity of Cu I (327.393 nm) on the liquid flow rate.

The sum of liquid flow rate of two channels was fixed at 1 mL min\(^{-1}\), and the ratio of the liquid flow rates of the channels was varied.
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Flow channel A: sample solution

Flow channel B: standard solution

Fig. 2  K. Ido et al.

Fig. 3  K. Ido et al.
Fig. 4  K. Ido et al.

Fig. 5  K. Ido et al.

Fig. 6  K. Ido et al.
Fig. 7  K. Ido et al.

Fig. 8  K. Ido et al.