Electrodialytic Enrichment and Matrix Conversion for the Determination of Trace Metals in Ultra-Pure Water

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ABSTRACT: The presence of trace contaminants in ultra-pure water (UPW) used in fabrication process can greatly affect the yield and quality of industrial products. In the present study, the electrodialytic enrichment of metal cations as a means of continuously monitoring the UPW quality was studied. A newly designed electrodialytic enrichment device (EED) was used to quantitatively transfer metal ions from samples to dilute nitric acid, which was then directly introduced into an inductively coupled plasma—mass spectrometry (ICP−MS) instrument. This process could be performed without contamination of the sample, and the enrichment factor was solely dependent on the flow rate ratio of the sample and acceptor solutions. The transference of analytes into the acidic solution improved the responsivity of the ICP−MS analysis, especially at low concentrations of less than 1 μg/L. Blank solutions to support the analysis of UPW could be produced using the EED effluent, from which metal ions were quantitatively removed. In addition, calibration curves with concentration ranges of several nanograms per liter were obtained by preparing standards using a dynamic gravimetric method while employing a single bottle and continuous mass monitoring to avoid any contamination from the volumetric flasks. The sensitivities associated with the ICP−MS analysis of a number of trace metal ions were improved by one or two orders of magnitude. The data show that the present EED is able to continuously produce enriched analyte solutions to allow the ongoing monitoring of UPW quality.

INTRODUCTION

Ultra-pure water (UPW) is widely used as a solvent for the preparation of standards and blanks in analytical protocols. UPW is also frequently employed in the semiconductor, pharmaceutical, and chemical industries and in nuclear power generation. The quality required for UPW varies depending on the situation, with semiconductor manufacture having the most stringent requirements. Water environmental contamination control requirements are less than 1 ng/L for some of the metal ions.1 At present, concentrations of such ions below 1 ng/L can only be reliably quantified using inductively coupled plasma−mass spectrometry (ICP−MS). The theoretical basis of ICP−MS, in which metals are ionized in a plasma and then detected using a mass spectrometer, was first established in 1980,2 and these instruments were commercialized in 1984.3 Since then, the sensitivity of ICP−MS has been improved based on the addition of various functions that eliminate the spectral interference of various polyatomic ions. Examples of these improvements include cold plasmas,4 high-resolution ICP−MS,5 and reaction/collision cells,6 which eliminate spectral interference by argon species decrease, increase mass selectivity, and remove polyatomic ions via reactions or collisions. In the latter case, the byproducts of reactions or collisions may also be removed based on kinetic energy discrimination (KED) effects.7 The recent commercialization of MS/MS instruments has also dramatically improved the limits of detections for various metals.8 However, even though sub-ng/L detection limits can be achieved using ICP−MS/MS, the sensitivity of conventional ICP−MS units has also been increased, so these instruments remain attractive as a means of continuously monitoring the quality of UPW. The sensitivity of ICP−MS depends on the analyte mass (equal to concentration × flow rate) introduced into the instrument. However, the extent to which the flow rate can be increased is limited because the efficiencies of the nebulization and ionization processes are both decreased at relatively high solution flow rates. Thus, analyte enrichment is the sole means of improving analytical sensitivity furthermore.

In the case of the conventional ICP−MS analysis of UPW, analyte concentration by evaporation is a common practice typically used9 and is typically performed in a quartz vessel that has been thoroughly cleaned to avoid contamination. The evaporation of water from a sample to obtain 1/100th of the original volume provides an increase of two orders of magnitude in analyte levels and can make it possible to determine sub-ng/L concentrations of metal ions. However,
this technique is labor intensive and can potentially introduce contaminants. The enrichment of metal ions can also be achieved using solid phase extraction or solvent extraction. Even so, the former techniques require pH adjustment, possibly leading to contamination, while the latter necessitates the use of organic solvents. Thus, neither method is ideal. On this basis, the present work examined the viability of employing an electrodialytic ion transfer device (ITD) to increase sensitivity during the analysis of UPW.

This electrodialytic ITD was initially developed for the pretreatment of sample prior to the analysis of ionic solutes. In this process, the ions in a sample are quantitatively and continuously transferred to separate acceptor solutions for cations and anions. This system has been applied to separate analyte ions from various sample matrices and to increase the concentrations of ionic solutes. Because the ITD quantitatively transfers ions from a sample to an acceptor solution, the concentration in the acceptor solution is determined by the sample-to-acceptor flow rate ratio. For the heavy metal cations, the flow rate ratio and enrichment factor equaled ×60 with a 1 μg/L standard solution. However, the enrichment could only be performed with the concentration levels of μg/L to mg/L because of the high background levels. This enrichment method has been applied to the analysis of chloroacetates (μg/L to mg/L concentrations) in tap water, which is typically employed using high-performance liquid chromatography (HPLC)–MS. In the present study, a newly designed ITD referred to as an electrodialytic enrichment device (EED) was employed to increase the concentration of metal cations in UPW to allow analyses at sub-ng/L concentrations. This method provides the benefits of “continuous” enrichment and a lack of potential for contamination because the EED is a closed system. The work reported herein involved increasing analyte concentrations via the EED in addition to an EED clean-up procedure that provided a lower blank signal. The preparation of blank samples for UPW analysis and dynamic gravimetric standard preparation were all included in this study.

The whole flow system for in-line enrichment of trace metals in UPW is drawn in Figure 1. The newly designed EED structure is shown in Figure S1. Sample UPW was continuously flowed into EED at 1 or 5 mL/min. Under the electric field in EED, metallic cations were transferred into 1 mM HNO₃ flowed at 0.1 mL/min quantitatively. Thus, metallic ions were enriched and introduced into ICP–MS via six-port injection valves. The blank generation with the EED sample effluent was also integrated into the flow system. See the Experimental Section for details of the present enrichment system.

RESULTS AND DISCUSSION

Electrodialytic Enrichment of Metal Cations. The enrichment performances were evaluated with inductivity coupled plasma—MS (ICP–MS) with the conditions summarized in Table S1. The selection of the mass-to-charge ratio is important, especially for ultra-trace analysis. Thus, we initially studied the selection of the mass-to-charge ratio (m/z). In the present study, we have used the KED mode for the removal of interference from the polyatomic ions such as Ar–C. The signal-to-noise ratio with a standard solution of 1 μg/L was obtained for various m/z of Cu, Fe, and Cr, which are well-known interfered elements by argon species (Figure S2 and Table S2). As a result, the m/z at the highest isotope ratio showed the best signal-to-noise ratio for all of the tested metals. The targeted sample in the present study is UPW, which does not contain the source of polyatomic ions. Thus, we choose m/z based on the highest isotope ratio. The used m/z in the present study is summarized in Table S3.

Initially, a 5-layer ITD apparatus employed in our previous work was used in conjunction with the analysis of UPW. For the trace concentration analysis, the stability of the blank signal is important. As an example, the limit of detection is calculated with the signal-to-noise ratio. Typically, the lower background signal is effective for the signal stability. The background signal is evaluated as a blank equivalent concentration (BEC), which is calculated as the concentration equivalent to the blank signal. The Cu²⁺ BEC for this device was determined to be 1200 ng/L after washing with a continuous flow of UPW overnight, which was too high to allow the analysis of trace-level metal ions at concentrations below the ng/L level. This high background concentration was thought to have possibility resulted from the cation-exchange membrane in the apparatus. The cation-exchange membrane is potentially contaminated with Cu²⁺. For this reason, the cation-exchange membrane and the one-solution layer used as the anion acceptor were removed, and the apparatus was redesigned to create the EED for the analysis of trace cations. The Cu²⁺ BEC obtained from this newly designed EED was much lower at 180 ng/L, representing a significant improvement.

The enrichment performance of the new four-layer EED was initially evaluated in trials using 25 elements each at a level of 0–250 ng/L (Figure S3). The data obtained for four of these elements from trials using concentrations of 0–1 μg/L prepared in UPW are also presented in Figure 2, in which the results obtained with and without the EED are compared. The 25 elements can be categorized into four groups based on the results. Ten of these elements (those highlighted in green in Figure S3 as well as Cr and Sr in Figure 2) show good...
agreement of the calibration curves with 10 times different y-axis scales. The newly designed four-layer EED incorporating AEM therefore provided suitable enrichment of these analytes. Four of the elements (highlighted in orange in Figure S3 as well as Cu and Pb in Figure 2) exhibited better linearity after the EED enrichment process. It should be noted that standards prepared in UPW directly introduced to the ICP–MS instrument without going through the EED enrichment had almost neutral pH values, although samples for the ICP–MS analysis are typically acidified so as to obtain accurate results, especially at trace levels. This may be caused by undesired adsorption on the tube walls. The effects of the acid concentration on the ICP–MS limit of detection are related to both the ionization potential of the analyte and the instrumental parameters. For these reasons, in a typical instrumental analysis, UPW is used as a BKS with a nominal pH caused these elements to form as hydroxides, because these ions are more likely to form non-ionic hydroxides than the others examined in this work. The distribution diagram of Bi(III) shows that the fraction of Bi(OH)₃ is >90% at pH higher than 6. Also, the same diagram of Ga(III) shows that the fraction of Ga(OH)₃ is maximum at pH 5.1. The pH of UPW is around neutral, and these species could not be effectively transferred as metal cations. The other elements highlighted in blue were affected by contamination. The limits of detection for these elements were determined based on the signal-to-noise ratios, so the actual sensitivity of the analysis was affected both by the extent of analyte enrichment and by the noise level. The latter was, in turn, determined by blank solution (BKS) analysis. All possible contamination sources were evaluated during this work, including EED itself and the volumetric flasks (VFs) used for standard preparation during the multi-element ultra-trace metal analysis.

**Decrease in Metal Elution from the EED.** Sources of metal ion contamination in the present work were investigated, and the most important source was determined to be the EED itself. As previously described, the redesign of the apparatus to the EED format dramatically decreased the extent of contamination, but the possibility of further decreasing the presence of metal contaminants was considered. As an initial step, a cleaning procedure was performed, during which voltage pulses (±20 V, 0.8 Hz) were applied for 12 h. These pulses generated higher current flow (~approximately 40 mA) compared with a constant voltage (2–3 mA) because the EED functioned as a capacitor (Figure S4). This higher electrical current effectively removed residual ionic solutes from the device without damaging the EED. The effects of this cleaning procedure are shown in Figure S5. The concentrations in the UPW were obtained by a factor of 10. A comparison of scenario A in Figure S5 (without the cleaning procedure) and scenario B (after applying the cleaning procedure) shows that 11 and 82% of Ni and Fe, respectively, were removed from the EED acceptor effluent. This effective removal of contaminants was obtained by generating a large current based on frequent switching of the voltage polarity. The cause of the different Fe and Ni removal efficiencies is not clear but can possibly be attributed to the different adsorption mechanisms of these two metals. The level of metal contamination in the effluent was also effectively decreased by replacing the carbon steel belt-punch previously used for making holes in the DM with the custom-made polyether ether ketone (PEEK) device. Following this change, the Ni and Fe levels were lowered to 6.5 and 8.9% of the original levels (scenario A), respectively (scenario C in Figure S5). The leaching from the DM was separately studied, and the Ni and Fe amounts released per unit surface area, with and without the use of the metallic belt-punch, were found to be 7.29/1.60 and 7.92/2.04 ng/cm², respectively. Interestingly, although the membrane was in contact with the metal punch for a very short time (approximately 1 s), this procedure introduced significant contamination. Further improvements were achieved by changing the DM material from regenerated cellulose to cellulose ester (CE). The used CE membrane was produced in a cleanroom environment and was processed free from heavy metals. This change led to a clear difference in the level of metal ion background in the EED effluent, giving 2.4 and 12% of the original levels for Ni and Fe, respectively (scenario D in Figure S5). Finally, repeating the voltage pulse cleaning of the improved EED reduced the Ni and Fe elution to 0.7% of the original value and below the limit of detection, respectively. These improvements were therefore employed in all subsequent trials.

**Blank Solution Preparation for UPW Analysis.** In many instrumental analyses, UPW is used as a BKS with a nominal analyte concentration of zero. However, in the present study, UPW was examined as though it were a sample. In initial trials, an in-line purification system based on a mixed-bed resin column (containing a mixture of cation and anion exchange
resins) was used to prepare BKS from UPW as a sample, while additional experiments used the EED effluent as the BKS. During this process, the EED transferred metal ions in the sample quantitatively to the acceptor solution, meaning that the effluent exiting the device should have been free of metals and suitable for use as BKS. The data obtained from both methods are summarized in Figure S6. The use of the EED effluent as BKS was lower than in-line purified with a mixed-bed resin column. The sample effluent from the EED contained nitrate ions transferred from the acceptor solution, so the output from the device was also passed through a mixed-bed resin column. In this newly developed system, the sample effluent from the EED was stored in a bottle that was protected from the ambient air, and the pump supplying the BKS (PP2 in Figure 1) drew from that container. These procedures decreased the metal concentration in the effluent acceptor solution in conjunction with a ×10 enrichment protocol. It was difficult to establish that the BKS represented metal-free UPW, but the BKS prepared using the present method did give reproducible data and the average relative standard deviation for the metal concentration was 6.5%. Thus, a BKS prepared from the EED effluent by using a mixed-bed resin column for purification was employed to establish signals with a concentration of zero in the present work.

**Dynamic Gravimetric Standard Preparation for Ultra-Trace Concentration Metal Ions.** As noted, the response obtained from the BKS solution was assessed. In addition, calibration curves were generated using standards having known concentrations. In the case of the calibration curves obtained without enrichment (Figure S3), some of the metals (such as Na, K, Ca, Mg, Fe, and Ni) did not give linear plots at the concentration levels of ng/L. Each calibration standard was prepared by dilution from a single mixed stock solution, and the majority of calibration curves generated without enrichment showed linear relationships. Nonlinear relationships are attributed to contamination stemming from the VFs used for standard preparations. These flasks were thoroughly washed with 1% nitric acid prior to use and employed only for specific concentrations, but even so it was challenging to avoid contamination completely. The most important issue was that the extent of contamination varied between flasks. VFs (25 mL) after washing were found to provide solutions containing 62.6 ± 14 and 322 ± 70 pg Cu and Fe, respectively. To avoid this effect, dynamic gravimetric standard preparation with a single bottle was instead employed. In this procedure, a container with a capacity of 1 L was placed on a digital balance, and its mass was monitored using a computer every 10 s intervals. The solution in this bottle was continuously introduced into the EED as a blank. Initially, the bottle was filled with UPW to ascertain the instrument response to an analyte concentration of zero for calibration curves. After a specific analysis time, varying amounts of the stock standard solution were added into the bottle, and the bottle was thoroughly agitated. The amount of solution added and the solution mass that remained in the bottle were both recorded on the computer such that the analyte concentration could be calculated. This gravimetric addition of the solution has been reported to be a more accurate approach to quantitation compared with the standard addition method.18 The prepared solution in the bottle was again introduced into the EED as a standard, and repeating this procedure allowed the system to be calibrated. This method was applied to evaluate the ×50 enrichment process using a 0–40 ng/L standard, and the resulting data are summarized in Figure 3. It should be noted that the present method was not a typical gravimetric solution preparation process. The “dynamic” gravimetric solution preparation used in the work reported herein employed a single bottle to avoid any contamination effects associated with the use of multiple containers and to allow accurate addition of the stock solution and continuous monitoring of the solution flow rate. The solution flow rates are important parameters in the EED because this device is based on the flow rate ratio, and this rate could be calculated from the mass changes of the container and the flow rate through the sample channel during the calibration procedure. This rate was determined to be 4.87 ± 0.11 mL/min.

**System Performance and Purified Water Analysis with EED Enrichments.** After establishing low contaminant levels in the blank solution and methods for preparing the BKS and trace-level metal in standards, the system performances were evaluated based on ×50 enrichment using the EED. The reproducibility was evaluated with a 500 ng/L mixed standard solution (Figure S7), and the averaged relative standard deviation for this was 2.5 ± 1.0% (n = 10). These results confirmed the suitable reproducibility of the EED system. Calibration curves for concentrations up to 25 ng/L were subsequently generated based on mixed standards prepared by the dynamic gravimetry method (Figure S8). Interestingly, the calibration curve of Bi showed good linearity at a concentration of <25 ng/L even though Ga did not. These phenomena can be explained by the effects of pH on the hydroxide species. Under neutral pH, Ga(OH)4− is formed16 and transferred into the anode side isolator solution or trapped by AEM. On the other hand, Bi(OH)4− is formed at pH higher than 10.5,15 and the removal of Bi3+ shifted the equilibrium of Bi species and quantitative transfer was achieved at relatively low concentrations. The details of the calibration equations, and correlation coefficients are also summarized in Table S3. Good linearity was observed in the case of those elements that could be detected (R2: 0.994–1.000). Table 1 provides the limits of detection associated with both ×50 enrichment and direct analysis and confirms that the present EED enrichment system dramatically improved the detection
The newly developed system was further applied to purified water analysis (Figure 4), and clear differences between purified water and UPW were observed. In the case of the UPW, the concentrations of most elements were less than the limit of detection, while all elements except Ba and Pb were detected in reverse osmosis-deionized water (RO-DI) and DI. Some of these elements were present at levels higher than 5 ng/L in these samples. The differences in analyte concentrations between the RO-DI and the DI may have been caused by the source water quality or the varying effectiveness of the RO process for each element.19 There were also differences between UPW samples obtained from three different UPW generators. The total metal concentrations in UPW samples 1, 2, and 3 were 10, 6.5, and 6 ng/L, respectively. The same source water was used for samples 1 and 2, but the purification cartridge employed to generate UPW 1 had been used longer than that used for UPW 2, while sample 3 was produced with a system intended for trace-level elemental analysis. Thus, even though the system employed to generate sample 3 had been used for a longer time span than the other two systems, this UPW had the lowest level of metal impurities. These results demonstrate that the EED system developed in this work could be applied for the evaluation of impurities in UPW.

**CONCLUSIONS**

The electrodialytic enrichment of metal cations as a means of evaluating the quality of UPW was demonstrated. This method permits ultra-trace-level elemental analysis based on the use of a newly designed EED and also allows blank solutions to be prepared along with standards via a dynamic gravimetric method. This technique is able to continuously generate enriched solutions and is thus well-suited to the continuous monitoring of impurities in UPW.

**EXPERIMENTAL SECTION**

Reagents. Nitric acid (ultra-pure grade, 68%, density = 1.42) was obtained from www.tama-chem.co.jp (TAMAPURE-AA-100). A standard solution containing 25 metal ions (ICP standard solution H) was obtained from www.kanto.co.jp. All reagents were prepared using UPW with a Simplicity UV system (SIMSV0000, www.merckmillipore.com).

**Electrodialytic Transfer Device for the Concentration of Metal Cations.** Figure S1 provides a detailed diagram of the EED used in this study, which contained four solution layers, separated by ion permeable membranes: two anion exchange membranes (AEMs) and a dialysis membrane (DM). The device also included solution channel gaskets with perfluoroalkoxy alkane (PFA) screens (opening of sieve: 204 μm, thickness: 100 μm, F-3220-04, www.flon-ind.com) immersed into Parafilm. These gaskets were prepared by cutting channel patterns on Parafilm with a CO2 laser cutting machine (Beamo, flux-japan.jp) followed by heated pressing with a PFA screen at 0.9 MPa and 40 °C for 5 min each, and the heated pressing process was repeated several times. The effective channel size was 5 mm wide by 40 mm long. Platinum mesh electrodes were placed on the top and bottom plates that

| Element | LODs (ng/L) | w/o enrichment | ×50 enriched | BEC (ng/L) |
|---------|-------------|----------------|--------------|------------|
| Li      | 153         | 3.80           | 0            |            |
| Be      | 118         | 0.94           | 0            |            |
| Na      | 213         | 0.08           | 0.44         |            |
| Mg      | 11.2        | 0.27           | 1.22         |            |
| Al      | 13.0        | 0.25           | 2.51         |            |
| K       | 668         | 0.26           | 1.88         |            |
| Ca      | 12.6        | 0.26           | 1.91         |            |
| Cr      | 2.36        | 0.10           | 0.76         |            |
| Mn      | 2.32        | 0.05           | 0.2          |            |
| Fe      | 19.1        | 2.55           | 11.52        |            |
| Co      | 2.03        | 0.01           | 0.08         |            |
| Ni      | 2.03        | 0.93           | 4.53         |            |
| Cu      | 8.78        | 0.23           | 1.46         |            |
| Zn      | 18.0        | 1.48           | 4.02         |            |
| Rb      | 2.70        | 0.04           | 0            |            |
| Sr      | 0.51        | 0.04           | 0.29         |            |
| Cd      | 2.71        | 0.02           | 0.09         |            |
| Cs      | 1.68        | 0.04           | 0            |            |
| Ba      | 1.43        | 0.15           | 0.73         |            |
| Pb      | 3.54        | 0.12           | 0.53         |            |
| Bi      | 11.0        | 1.10           | 3.75         |            |

The LODs without enrichment were obtained with the mixed standard solution prepared with 1 mM HNO₃. None of the method described in the present study was applied.

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Figure 4. Results from the analysis of UPW with ×50 enrichment using the EED. RO-DI: reverse osmosis-deionized water, DI: deionized water, UPW: ultra-pure water.
bracketed the device, and the membranes and gaskets described above were sandwiched between these two plates, after which the plates were fastened using screws tightened to a 20 cN·cm torque. The resulting EED was cleaned by applied voltage pulse, while UPW flowed through all the channels at a rate of 0.20 mL/min. The voltage pulses (±20 Vp-p) were generated by the amplification of a square wave function generator signal (10 Vp-p, 0.8 Hz) using a high-power operational amplifier (OPA511PA, www.ti.com). This procedure was repeated for 24 h. The cleaned EED was stored in a thoroughly cleaned container made from polypropylene.

Flow System. A flow diagram of the EED is presented in Figure 1. During the operation of this device, a sample solution was pumped at a rate of 5.0 mL/min by a peristaltic pump (PP1, MP-2000, ssleyela.co.jp) through a poly(vinyl chloride) PVC pumping tube (2.29 mm inner diameter) and introduced into the EED via two of the three-way solenoid valves with the poly(tetrafluoroethylene) contact surface (SV1 and 2, MTV-3-1/4UFH-3, takasago-elec.co.jp). The effluent from the EED sample channel, from which cations had been quantitatively removed, passed through valve SV4 and was collected in a reservoir for subsequent use as a blank solution. The solution in this reservoir was impelled by pump PP2 via valves SV3 and SV2 into the EED sample channel during the analysis of the system blank. Each of the solenoid valves was switched as required by a sequencer (ZEN-10C3AR-A-V2, www.fa.omron.co.jp). The highly pure nitric acid (1 mM) was introduced into the acceptor channel of the EED via a column filled with a cation-exchange resin by a double plunger pump having a PEEK head (PLP1, KP-22-01, www.flohm.co.jp). The EED acceptor effluent was directly introduced into a PEEK tubing sample loop (0.75 mL, 1.0 mm inner diameter) in preparation for the injection of a sample for ICP–MS analysis. The 1 mM HNO3 carrier solution used to introduce the sample onto the ICP–MS was pumped at a flow rate of 0.75 mL/min using a double plunger pump (PLP2). The EED isolator solutions were impelled at a flow rate of ~2 mL/min by a Unimor pumps (UP1 and UP2, UPS-112E, www.nitto-kohki.co.jp). Each solution other than the sample was subjected to an in-line cleaning process as it passed through the cation or mixed-bed exchange resin column.

Standard Preparation for Ultra-Trace-Level Calibration. In the present study, standards having ultra-low analyte concentrations (<100 ng/L) were prepared gravimetrically. Common VFs could not be used to prepare these standards accurately because the leaching from the flasks affected the metal concentrations in the standards. Consequently, a newly developed dynamic gravimetric method was employed for standard preparation. In this cleaning process, a thoroughly cleaned 1.0 L PFA bottle was filled with UPW, and this water was replaced weekly for a 1 month period. The fresh UPW-filled bottle was placed on an electric balance (EK-4100i, www.aandd.co.jp) connected to a computer that recorded the mass reading from the balance at 10 s intervals. The mass readings were used for calculating the solution flow rate and the concentration of the standards. The UPW in the bottle was subsequently introduced into the EED sample channel as a blank initially. After obtaining the blank signal, a small amount of a 2 μg/L stock solution was added to the bottle, after which the bottle was agitated and again placed on the balance.

Metal Cation Analysis. Metal cations were analyzed using an ICP–MS instrument (iPAQ RQ, www.thermofisher.com). During these trials, enriched samples were assayed using the flow injection analysis mode as previously described. The ICP–MS parameters are summarized in Tables S1 and S3. The entire apparatus was contained in a home-made clean booth (750 mm × 3000 mm × 900 mm) with an attached high efficiency particulate air (HEPA) filter and particle counter integrated air purifier (PMMS-DC-100, www.irisohyama.co.jp).

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00648.

Structure of the EED, ICP–MS analytical conditions, effects of the mass-to-charge ratio on the signal-to-noise ratio, preliminary experimental results based on multi-element enrichment trials, current–voltage relationship in the cleaning procedure, effects of the cleaning procedures, relative responses obtained with specially prepared blank solutions, system reproducibility data, calibration curves obtained with X5 enrichment, and equations and correlation coefficients for the calibration curves (PDF)

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Notes
The authors declare no competing financial interest.

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