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Ultratrace Determination of Selenium by Hydride Generation–Inductively Coupled Plasma Mass Spectrometry Operated Under Nonrobust Plasma Conditions

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Abstract: A hydride generation–inductively coupled plasma mass spectrometer (HG-ICPMS) operated at low RF power (720 W) was demonstrated to be suitable for ultra trace determination of Se, which is an element with high ionization potential (IP). ^{78}Se analysis free from $^{38}\text{Ar}^{40}\text{Ar}$ spectral interference was achieved by operating the plasma under a so-called warm plasma condition (as opposed to traditionally defined hot and cool plasmas). In this warm plasma, there is a sufficient population of energetic Ar^+ to ensure ionization of Se, while the number of $^{38}\text{Ar}^{40}\text{Ar}$ ions is at the minimum, due to the dimer's bimodal profile. A detection limit of 1 ng/L was achieved for ^{78}Se . Background spectra of warm and hot plasmas were compared. Two types of HG gas–liquid separators were compared. The technique was applied to measure trace amounts of Se in atmospheric samples; namely, cloud water and aerosol particulate. Good agreement was found between HG warm plasma ICPMS and pneumatic micronebulization hot plasma ICPMS for the cloud water samples. The water extract of aerosol particulate typically contained 50–100 ng/L of Se, equivalent to 0.25–0.5 ng/m³ in the atmosphere. Ours appears to be the first report of the use of nonrobust plasma ICPMS for a high-IP element; the superb accuracy and sensitivity of this technique rival those of other powerful

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trace analytical methodologies such as HG-LIF, HG-LEI, or DRC-ICPMS. It is conceivable that warm plasma ICPMS is applicable to other elements with high IP.

Keywords: Ultratrace determination of selenium, ICPMS, hydride generation, warm plasma ICPMS

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICPMS) is a powerful method for trace determination of elements in various sample matrices. It is a sensitive and multielement analytical method capable of sub-ng/L detection limits. However, the technique is prone to spectral and nonspectral interference. Spectral interference includes isobaric interference, caused by those interfering elements that have the same m/z values as the analytes, and polyatomic interference, caused by matrix-induced molecular species (oxides, argides, nitrides, dimers, etc.). The nature of most of these interferences has been studied and a variety of techniques, (e.g., cool plasma,^[1] shield torch,^[2] collision cell,^[3] dynamic reaction cell,^[4] solvent removal,^[5] and high-resolution mass spectrometer,^[6] have been developed to counter the problems. Nonspectral interference refers to the matrix-induced signal intensity changes regardless of the presence of spectral components. This interference is due to matrix-induced factors, which exert an influence on sample transportation, ionization in the plasma, ion extraction, or ion throughput in the resultant ion beam. The interference normally results in suppression,^[7] although sometimes in enhancement,^[8] of the analyte ion signal as the concentration of matrix increases.

When an unbalanced load coil is used, a shield torch can be combined with lower plasma power (cool plasma), higher nebulizer flow, and larger sampling depth, to suppress the polyatomic argide ions. This opens the possibility for determination of K, Ca, and Fe without substantial interference from Ar^+ or ArH^+ . Although cool plasma conditions allow the determination of elements with low ionization potentials (IPs), the method's sensitivity declines significantly for elements with high IPs, as the ionization temperature and electron density in the source plasma drop. In direct injection high-efficiency nebulization ICPMS, Minnich et al.^[9] observed that the detection limits of Se and As worsened by factors of 1.5 and 500, respectively, when cool plasma was used. Tanner^[10] concluded that the cooler plasma yielded sensitivities that were 2 to 3 orders of magnitude lower for elements having IPs of 7 to 8 eV and 3–4 orders of magnitude lower for elements with IPs above 9 eV. Se (IP = 9.75 eV) is among those elements that would suffer severe loss of sensitivity in the cool plasma.

Trace determination of Se has profound implications in biologic, environmental, geologic, and toxicologic applications. It is an element either essential or toxic to human health, depending on the concentration present in the

body.^[11] Therefore, accurate determination of Se at trace level is essential to the diagnosis and treatment of diseases. In environmental science, Se has been used as a tracer for the study of transportation and transformation of pollutants in the atmosphere.^[12,13]

The current work was undertaken to explore the possibility of extending the benefits of the use of cool plasma to this “difficult” yet important element. To accomplish this, we coupled a hydride generation (HG) sample introduction system to an ICPMS. HG improves analytical sensitivity by eliminating the spray chamber and hence reducing analyte loss during sample transportation to the ICP torch. By separating the elements of interest from the sometimes complex sample matrix, HG reduces matrix effect and plasma loading and hence increases sensitivity and selectivity. ⁷⁸Se is about three times more abundant than ⁸²Se, but ⁷⁸Se’s detection is hindered by the much more highly populated ³⁸Ar⁴⁰Ar dimer in a hot plasma. The key to success is finding a plasma that is hot enough to adequately ionize Se for strong ion counts yet cool enough to prevent the ³⁸Ar⁴⁰Ar from swamping the ⁷⁸Se signal (i.e., a “warm” plasma is needed). The operating conditions of HG and ICPMS were carefully optimized. Spectral features taken from plasmas under different conditions were compared. Two HG configurations were investigated, and detection limits were compared. The use of internal standards to accommodate the signal drift was explored. Real environmental atmospheric samples were analyzed for Se with concentration ranging from 50 ng/L to 30 µg/L, and the results were verified by micronebulization hot plasma ICPMS.

EXPERIMENTAL

The ICPMS is an HP 4500 (Agilent Technologies, Wilmington, DE, USA) equipped with a ShieldTorch system, ChemStation software, a HG integrated sample introduction system (HG-ISIS), and an ASX 500 auto sampler (Cetac Technologies, Omaha, NE, USA). The plasma gas and auxiliary gas flows were respectively fixed at 16 L/min and 1.0 L/min. For verification of the results from HG, a micronebulization auto sampler (ASX 100; Cetac Technologies) replaced the HG-ISIS and ASX 500 auto sampler for sample introduction.

Chemical reagents included concentrated HCl acid (AR Select; Mallinckrodt Baker, Phillipsburg, NJ, USA), selenium calibration standards and independent QCs diluted from 1000 mg/L NIST traceable standards (Inorganic Ventures, Lakewood, NJ, USA and SCP Science, Champlain, NY, USA, respectively), natural water SRM 1640 (NIST, Gaithersburg, MD, USA), NaOH (pellets, 99.99%; Aldrich, Milwaukee, WI, USA), and NaBH₄ (99%; Aldrich). The Se hydride generating chemicals (HCl acid, NaOH pellets, and NaBH₄) had been tested to contain extreme low concentration of Se impurity. Other grades of the same chemicals may contain substantially more Se impurity to ultimately affect limit of detection.

On August 2, 2001, aerosol particulate and cloud water samples were collected simultaneously from a remote rural area (Whiteface Mt., NY, USA). The aerosol particulate samples were collected on Teflon filters. The sampling time was 5 min, during which about 0.4 m^3 of air was pulled through the filter. Cloud water was collected in the same time interval, by the use of an ASRC omnidirectional cloud water collector into precleaned polyethylene bottles.^[14] The samples were filtered through an $0.4\text{ }\mu\text{m}$ filter and acidified to contain 0.15% of Ultrex HNO₃. Both the aerosol and cloud water samples were stored at 4°C until analyzed. Before the analysis of trace metals, the aerosol particulate filter was placed into a test tube, and 7.0 mL of deionized water was added. The tube was placed in a 75°C ultrasonic bath for 2 hr to allow extraction of Se into the solution, of which 2.0 mL was taken and mixed with 2.0 mL of concentrated HCl. The same volume of cloud water sample was taken and mixed with 2.0 mL of concentrated HCl. The solutions were then heated in a water bath at 80°C for 25 min, along with the calibration and QC solutions, to reduce Se(VI) to Se(IV). NaBH₄ solution (in 0.05% w/w NaOH) was used as the reducing agent for HG. This digestion and reduction procedure was developed only for the types of environmental samples studied here. For speciation and/or total recovery of Se in other types of samples that may contain complex matrices, further pretreatment methods may be needed.^[15,16]

RESULTS AND DISCUSSION

Hydride Generation ICPMS

Shield torch cool plasma ICPMS has been discussed extensively elsewhere.^[1,2,10,17] A plasma operated under "cool" condition may be more subject to matrix effect because the plasma is no longer "robust." However, the coupling of HG as a sample introduction tool to the system provides an opportunity to overcome this problem, as only the analyte of interest is introduced into the plasma in the form of a gas (provided that there is little of any other hydride element in the sample, which is usually true for atmospheric aerosol samples) leaving behind the matrix as the waste. In a normal (hot) plasma, ⁷⁸Se isotope is usually not the first choice for detection, because it suffers severe spectral interference from ³⁸Ar/⁴⁰Ar dimer. More often, ⁸²Se isotope is used for detection; however, its abundance (8.73%) is only about one-third that of ⁷⁸Se. With the shield torch-cool plasma system, both isotopes can be detected at trace levels. This not only enhances the sensitivity by measuring Se via a more abundant isotope, but it also reduces spectral interference because the plasma conditions are now allowed to be adjusted to maintain the ⁷⁸Se/⁸²Se ratio close to the theoretical value.

Comparison of Two Gas–Liquid Separators

Two types of gas–liquid separators are shown in Fig. 1. Similar devices have been used in tandem with atomic absorption and ICP optical emission spectrometry.^[18] Nevertheless, a limited amount of information is available when they are coupled with the much more sensitive ICPMS. Major differences between the separators exist in volume, sensitivity, and carryover effect, resulting in a difference in limits of detection. In type I, the gas–liquid mixture is introduced into the bottom chamber of the separator by a concentric nebulizer, which breaks down liquid into aerosol to allow sufficient separation between the hydride gas and the solution. The hydride gas then passes through a Teflon filter and enters the upper chamber and subsequently the ICPMS. The type II adopts a simple flow-over approach: the gas–liquid mixture flows in from one side, the liquid is pumped out from the other side, and the hydride gas bubbles out of the solution and eventually enters the ICPMS. Our preliminary study demonstrated (data not shown here) that the simple flow-over design in the type II is sufficient to separate the hydride from the liquid; the concentric nebulizer used in the type I separator did not yield better sensitivity. Volume and surface area are much less in the type II separator than those in the type I; thus, the type II separator is less prone to carryover effect and loss of sensitivity due to dilution. In the type I, aerosols generated by the nebulizer are suspended in the chamber, and this prolongs the washout time. The fine portion of the aerosols may penetrate the Teflon filter and enter the ICPMS, resulting in matrix interference and in increase of plasma loading, and thus reducing sensitivity. For these reasons, the ion counts of the Se in the type II setup was twice as high as that in the type I when the same solution was analyzed. It took about 60 min for the type I separator to rinse out the residue of a

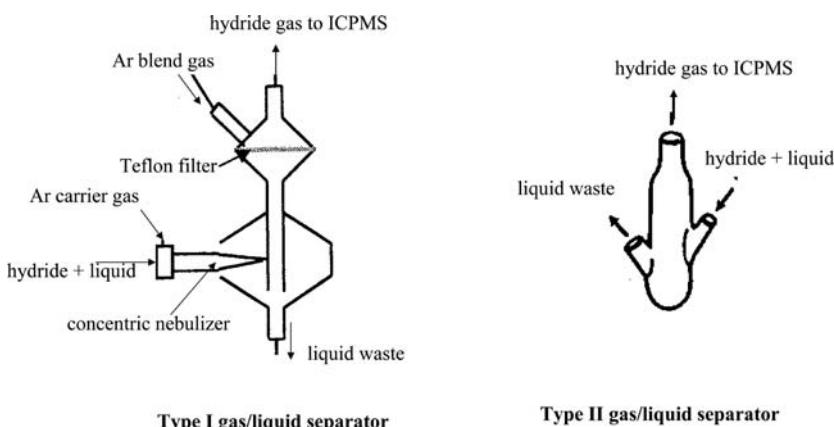


Figure 1. Two types of gas–liquid separators used for hydride generation ICPMS.

20 $\mu\text{g/L}$ Se solution but only 10 min for the type II. When the Se concentration was kept under 0.5 $\mu\text{g/L}$, 3 min of total rinse time was usually sufficient to bring the background to the blank level for the type II separator. Therefore, the type II separator is more suitable to couple with ICPMS for trace analysis of Se; it was accordingly used to finish the rest of the study.

Optimization of Plasma Conditions

The sample and reductant uptake rates were optimized to be 1.7 mL/min and 1.2 mL/min, respectively. The reductant (NaBH_4) concentration was optimized to be 0.2% (w/w). The parameters were optimized for both Se and Te at two concentrations (0.2 and 2 $\mu\text{g/L}$) to represent low and high concentrations in real samples. The tuning solution was 2 $\mu\text{g/L}$ Se in 6 M HCl. Se has major isotopes at $m/z = 76, 77, 78, 80$, and 82; argon dimers contribute strong interference to $m/z = 76, 78$, and 80 when the plasma is hot. The criterion for optimization of the plasma for Se measurement is to minimize the ion counts from interfering species, mainly from the argon dimers, while maximizing the counts from the Se isotopes. When the ion count ratio between two Se isotopes is equal to the theoretical value, the plasma condition is then considered optimized. Figure 2 plots the

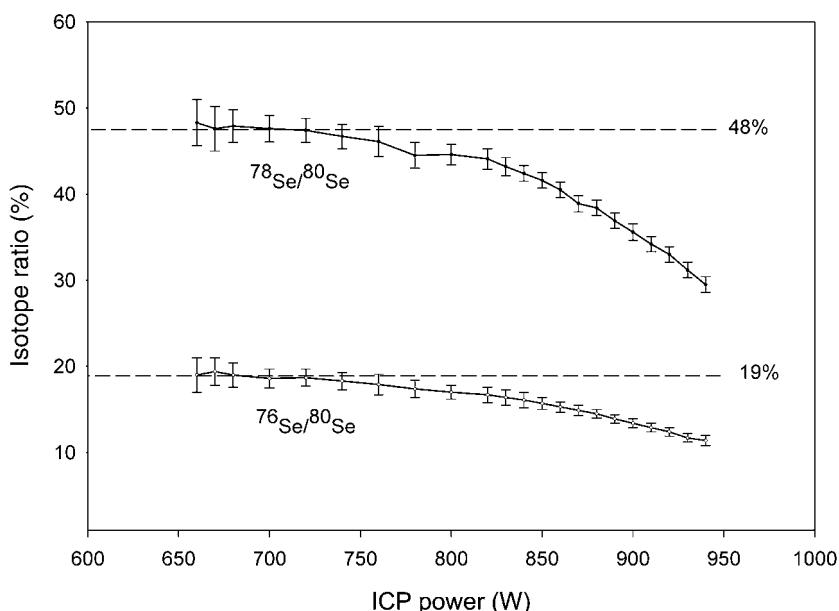


Figure 2. Se isotope ratio versus ICP RF power. The error bars represent the standard deviation of three repeat measurements.

Se isotope ratios versus the ICP RF power. The theoretical values are marked with dashed lines. Other instrumental conditions were fixed as follows: carrier gas = 1.47 L/min, sampling depth = 7 mm, RF matching = 2 V, Torch-H = 0 mm, and Torch-V = 0.1 mm. There is an RF power threshold at 720 W, above which the Se isotope ratio is less than the theoretical value, indicating significant spectral interference from Ar_2^+ ; under which the Se isotope ratio is equal to the theoretical value, indicating minimal spectral interference from Ar_2^+ . The isotope ratios are maintained at theoretical values when the RF power is less than the threshold power, but the signal becomes weaker and the precision poorer, resulting in higher detection limits. The ratios decrease monotonically when the RF power is increased, indicating that the number of $^{40}\text{Ar}^{40}\text{Ar}^+$ ions outpaces that of Se isotopes, and that the interfering species (argon dimers) is exerting significant effects on the Se signal. The two plots show identical threshold power at 720 W. Plots (not shown) of two other isotope ratios ($^{77}\text{Se}/^{80}\text{Se}$ and $^{82}\text{Se}/^{80}\text{Se}$) revealed a similar pattern and the same threshold power. For best analytical results, the optimum RF power would be the threshold power at which the signal-to-noise ratio is the highest and spectral interference is kept minimal (i.e., the warm plasma condition). The threshold power that is used to define warm plasma may change with the changing of other parameters, most notably the rate of carrier gas. A different plot of isotope ratio versus RF power can be drawn for a different carrier gas flow rate; the threshold power decreases with the decrease of carrier gas. However, the plasma becomes unstable or even extinguished when it is operated below RF 680 W, as a result of the air uptake from the sampling probe being exposed to the air when moving from one solution to another.

Background Spectra

Figure 3 shows the background mass spectra obtained under hot (Fig. 3A) and warm (Fig. 3B) plasma conditions. Blank HCl (6 M) solution was mixed with 0.2% NaBH_4 to generate hydride. The operating parameters for warm plasma were kept the same as those described in the previous section. For the hot plasma, the RF power was raised to 900 W while other parameters were kept the same. As far as the Se measurement is concerned, one can see a substantial reduction of $^{38}\text{Ar}^{40}\text{Ar}$ in the warm plasma; this leads to the lowering of background and hence the improvement of detection limit. However, high level of ion counts were seen at m/z = 20, 21, and 30 in the warm plasma perhaps due to OH_2^+ , OH_3^+ , and NO^+ . The mechanism probably involves the production of neutral H_2O and NO and subsequent ionization via ion-molecule chemistry when the RF power is reduced. Other researchers have also seen the similar shift of dominant ions from Ar-derived species to H_2O^+ and NO^+ derived species.^[10]

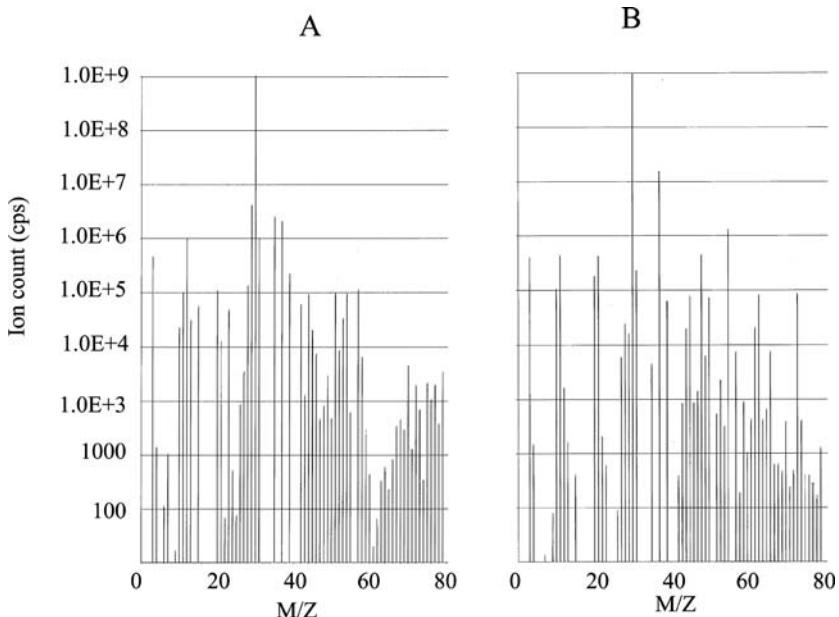


Figure 3. Background spectra for (A) hot and (B) warm plasma hydride generation ICPMS.

Long-term Drift and Internal Standard

The long-term stability of the Se signal is shown in Fig. 4, along with Te, As, Sb, and Bi as potential internal standards (ISs). For the time being, we will ignore the fact that As may be present in environmental samples in a significant amount to invalidate its candidacy. For a period of 105 min, the ion counts of ^{78}Se (2 $\mu\text{g/L}$) and ^{130}Te (0.2 $\mu\text{g/L}$) increase monotonically by 84% and 82%, respectively. The overall relative standard deviation (RSD), 18%, is identical for the two isotopes. ^{75}As (200 $\mu\text{g/L}$) also shows an upward trend, but at a slower rate, increasing by 36%, while the overall RSD is 10%. ^{209}Bi (0.01 $\mu\text{g/L}$) remains constant, with an overall RSD of 5%. ^{121}Sb (10 $\mu\text{g/L}$), however, shows a downward trend; its ion count drops by 72%, with an overall RSD of 36%. Obviously, Bi and Sb are not suitable ISs for Se, as they show a different drift trend; hence, they were immediately eliminated as candidates. As and Te merited further investigation: the ratios between As, Se, and Te were determined and plotted. Systematic drift can still be seen for $^{130}\text{Te}/^{75}\text{As}$ (drift by 25%, with RSD = 8%) and $^{78}\text{Se}/^{75}\text{As}$ (drift by 26%, with RSD = 9%), although the overall drift is smaller than that of individual element. ^{130}Te and ^{78}Se appear to “lock steps” with each other: there is no apparent drift on $^{130}\text{Te}/^{78}\text{Se}$ with RSD = 3%, which is significantly smaller than the RSD of the individual element. The rule of thumb in

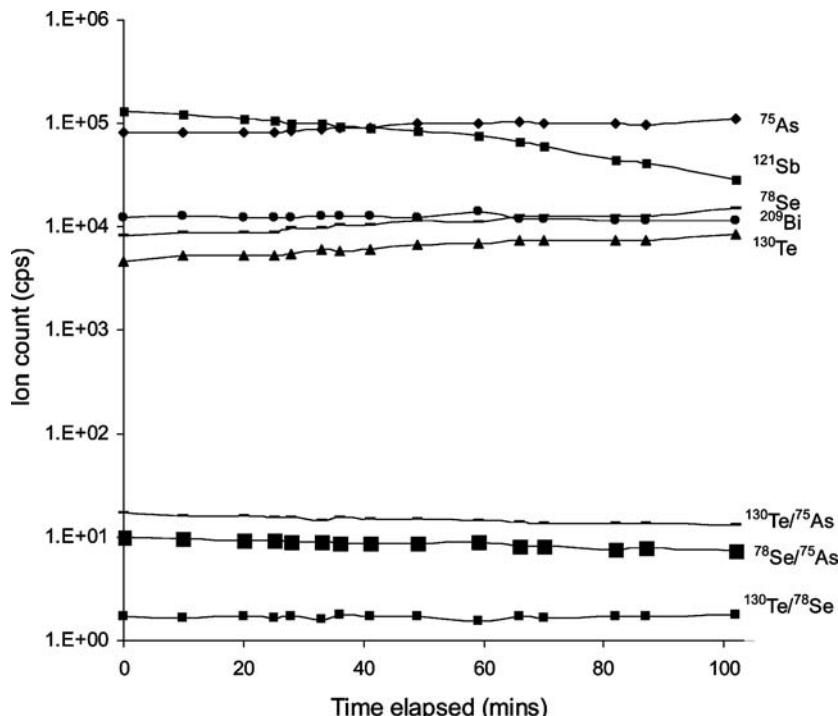


Figure 4. Patterns of signal drift for As, Se, Sb, Bi, and Te. Te is the best internal standard for Se.

selecting an IS is to match its IP and mass with those of an analyte, because the ionization process in the plasma and the ion trajectory in the mass analyzer are the most common sources of disparity between the IS and the analyte. Therefore, we would expect that ^{75}As (IP = 9.81 eV) is better than ^{130}Te (IP = 9.01 eV), for use as an IS for ^{78}Se (IP = 9.75 eV). Nevertheless, the ratio between ^{130}Te and ^{78}Se yielded the least drift and the lowest RSD (3%). This indicates that the major source of signal drift is not from the disparity in ionization process in the plasma or the ion trajectory and detection in the spectrometer but from what occurs in analytes prior to their being introduced into the plasma. The most likely cause is the hydride reaction, whose efficiency is dependent on the chemistry of the individual analyte and on the chemical and physical parameters of the reaction.^[19] Te and Se both belong to group 6B of the Periodic Table, and they show similar chemical characteristics in their reaction with various chemicals. Therefore, any change in the parameters of the hydride reaction would likely affect the two elements similarly, resulting in similar ion count responses on the ICPMS. Therefore, Te was used as an IS throughout. We do not know what has caused the change of the condition of the hydride

reaction. However, the temperature was observed to increase slightly during the course of the experiment, due to the heat emitted from the vacuum pumps. An air conditioner had been installed in the laboratory, but it was apparently insufficient to offset the heat buildup.

Detection Limits

Calibration curves (not shown) obtained from a hot and a warm plasma were both linear ($R^2 > 0.9999$) for at least 5 orders of magnitude, even though they had only been calibrated up to $0.5 \mu\text{g/L}$ for sample analysis, because of the concern of carryover. The intercept, which represents the background ion counts, is more than 130 times higher in hot plasma than in warm plasma, while the slope, which represents the analytical sensitivity, is only twice as steep. The detection limit is defined as the concentration equal to three times the standard deviation of 12 measurements (ion counts) of a blank solution (6 M HCl). We have seen from previous discussion that HG is prone to both carryover contamination and long-term signal drift; these issues were addressed in the detection limit experiment. In addition to the use of Te as IS, we evenly spaced the 12 blank measurements into a typical 8-hr analytical sequence, which included calibrations, samples, and QCs. To keep the carryover low, the highest calibration or QC was $0.5 \mu\text{g/L}$. No sample concentration exceeded the calibration range. Detection limits were calculated to be 45 ng/L and 1 ng/L for the hot and the warm plasma, respectively. With its high IP value (9.75 eV), Se is normally analyzed under hot plasma conditions for higher ionization efficiency. The drawback is that the elevated background degrades the detection limit. Cool plasma lowers the background, but the sensitivity suffers a loss of 3–4 orders of magnitude, due to the reduction in energetic source ion such as Ar^+ . In warm plasma, the energetic Ar^+ population is high enough to yield sufficient ionization for Se, whereas the interfering species, namely Ar_2^+ , is produced at the lowest efficiency, due to its bimodal profile.^[10] this dimer's population peaks at both low and high plasma powers and reaches a trough at intermediate power (warm plasma). We believe that we have identified the warm plasma conditions at which high ion counts are produced for Se with minimal interference from argon dimers.

Comparison with Other Techniques and Applications

The detection limit for Se measured by HG warm plasma ICPMS rivals those by other highly sensitive techniques, such as laser-induced fluorescence (LIF), laser-enhanced ionization (LEI), and dynamic reaction cell ICPMS (DRC-ICPMS). Table 1 lists the detection limits of Se obtained by various techniques. Santosa et al.^[20] used an HG-hot ICPMS system to obtain a 0.5 ng/L detection limit for Se by measuring isotope ^{82}Se . ^{82}Se is free from

Table 1. Comparison of the Se detection limits by various trace metal techniques

Technique	Detection limit (ng/L)	Isotope	Reference
HG-ICP (warm) MS	1	78	This work
HG-ICP (hot) MS	0.5	82	20
DRC-ICPMS	5	82	22
LEI	6	N/A	23
LIF	0.5	N/A	24
Pneumatic nebulization ICPMS	60	82	Our lab

HG, hydride generation; ICPMS, inductively coupled plasma mass spectrometer; DRC, dynamic reaction cell; LEI, laser-enhanced ionization; LIF, laser induced fluorescence.

Ar_2^+ interference and thus is suitable for hot plasma, at which higher sensitivity can be achieved. However, ^{82}Se is prone to isobaric interference from Kr, which is an impurity in argon. From our experience, the interference magnitude from Kr appears to increase with the depletion of liquid argon in the tank, resulting in baseline drift and poor accuracy at low concentrations. In our study, ^{82}Se seems peculiarly prone to positive bias in environmental samples. For example, the analysis of the SRM1640, a NIST Nature Water Standard (target value = 220 ng/L after 100 times dilution), yielded 95% and 130% recoveries for ^{78}Se and ^{82}Se , respectively. Polyatomic interference from $^{82}\text{SO}_3^+$ and/or $^{82}\text{HBr}^+$ may contribute to the bias because SO_4^{2-} (acid rain) and Br are common in natural water. HG should have drastically reduced the amount of water solvent in the plasma; thus, the amount of SO_4^{2-} and Br that entered the plasma with the water solvent is expected to be minimal. Nevertheless, volatile S and Br components might have been generated along with Se hydride, resulting in the polyatomic spectral interference.

DRC-ICPMS was designed to remove polyatomic interference through specific ion-analyte reactions.^[21] This instrument is commercially available, and its detection limit for Se is 5 times higher than that done in the current work.^[22] Pacquette et al.^[23] achieved Se detection limits of 0.5 ng/L and 6 ng/L by the use of flame HG-LIF and HG-LEI, respectively. Comparable detection limits were achieved when the electrothermal atomizer-LIF technique was used.^[24] Regular pneumatic nebulization ICPMS yielded a detection limit of 130 ng/L.^[25] This high value was due to a combination of low transportation efficiency of analyte from the spray chamber to the plasma and the unavailability of ^{78}Se as the analytical isotope in a hot plasma environment. The detection limit should be improved when a micronebulizer is used because of the increase of transportation efficiency and the reduction of sample load in the plasma.

We applied HG warm plasma ICPMS to the determination of trace levels of Se in aerosol particulate and cloud water samples. The typical Se

concentration in the water extract of the aerosol particulate was 50–100 ng/L, equivalent to 0.25–0.5 ng/m³ in the atmosphere. The accuracy of the calibration was assessed by measurement of a 50 ng/L Se solution diluted from an independent source (SCP Science) and a 100-times diluted SRM 1640 solution, with the Se concentration being 220 ng/L after the dilution. The recoveries were 98% and 101%, respectively, with RSDs less than 2% obtained from 10 replicates. No independent verification on the aerosol samples was done, due to the lack of other analytical method applicable to such low concentrations. Nevertheless, the concentrations of Se in cloud water samples were verified using micronebulization ICPMS operated under hot plasma condition. Twenty-seven cloud water samples were collected between 8:45 a.m. and 10:55 a.m. at the summit of Whiteface Mt. on August 2, 2001. The samples were diluted 100 times when analyzed by HG–warm plasma–ICPMS for the best results because the carryover effect was minimized. The samples were analyzed without dilution when tested by micronebulization ICPMS. The Se concentrations range between 4 and 30 µg/L. These two sets of measurements in general show excellent agreement: when a percentage ratio between the value measured by micronebulization ICPMS and that measured by HG–warm plasma–ICPMS was taken, the average percentage was 97% with a RSD of 7%; no apparent positive or negative bias was seen. Twenty-four out of the 27 measurements agreed to within $\pm 10\%$. Among the three with $>10\%$ differences, two showed negative bias, at 86% and 81%, respectively, while one showed positive bias at 122%. Figure 5 shows the linear regression between these two sets of results; the slope and R^2 are 0.94 and 0.97, respectively. The data show that HG-ICPMS operated under warm plasma condition is capable of the same accuracy as pneumatic ICPMS but with a much improved detection limit. Its superior sensitivity is essential to the accurate measurement of trace levels of Se in a variety of samples such as the water extract of small amounts of atmospheric aerosol particulates demonstrated here.

CONCLUSIONS

We have demonstrated that Se, an element with high IP, can be successfully determined at trace level in a nonrobust plasma condition by ICPMS. We optimized the experimental conditions for HG and warm plasma ICPMS. In a warm plasma, the ionization efficiency for Se remains high, while the spectral interference from $^{38}\text{Ar}^{40}\text{Ar}$ is minimal due to the bimodal profile of the argon dimers. Two types of HG gas–liquid separators were compared: the simple flow-over type (type II) proved to be a better design for ICPMS in terms of higher sensitivity and less carryover. Tellurium was found to be the best IS for correcting signal drift. The detection limit was determined to be 1 ng/L after the operation conditions had been optimized. This technique was applied to measure trace amounts of Se in environmental atmospheric

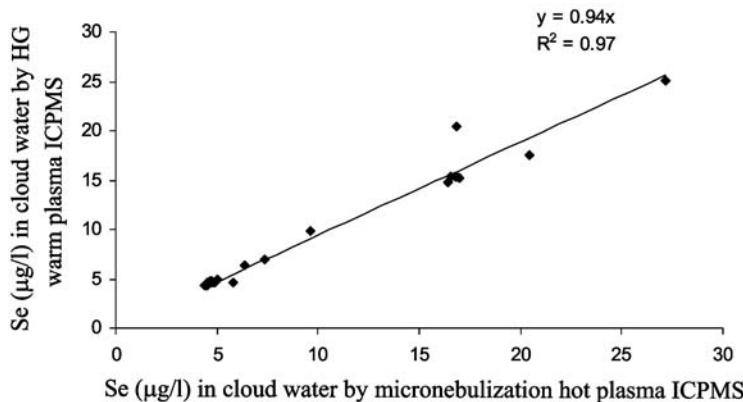


Figure 5. Linear regression between the two sets of Se concentration ($\mu\text{g/L}$) measurements in cloud water samples.

samples, namely cloud water and aerosol particulate. Good agreement was found between results from HG–warm plasma–ICPMS and pneumatic micro-nebulization ICPMS. Based on our search of the literature, this is the first report of the use of nonrobust plasma ICPMS for a high IP element (Se), achieving an accuracy and a sensitivity that are equivalent to or better than those of other powerful trace analytical instruments such as HG-LIF, HG-LEI, or DRC-ICPMS. It is conceivable that warm plasma ICPMS will be applicable for other elements with high IP.

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