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Accurate and Precise Determination of Silver Isotope Fractionation in Environmental Samples by MC-ICP-MS

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Abstract

High precision silver isotope ratios in environmental samples were determined by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). Purification of Ag from sample matrices was performed by a two stage tandem column setup with use of anion and cation exchange resin, sequentially. It was found that a 1 % HNO₃ and 3 % HCl was efficient to stabilize Ag in the final purified sample digests prior to MC-ICP-MS determination. Pd at 2 µg g⁻¹ was added to both sample and Ag standard solution as a common doping matrix as well as an internal standard for mass bias correction. Mass discrimination and instrument drift were corrected by a combination of internal normalization with Pd and standard-sample-standard bracketing, without assuming identical mass bias for Pd and Ag. NIST SRM 978a (silver isotopic standard reference material) was used for method validation and subjected to column separation and sample preparation processes. A value of -0.003 ± 0.010 ‰ for $\delta^{107/109}\text{Ag}$ (mean and 2SD, n=4) was obtained, confirming accurate results can be obtained using the proposed method.

To the best of our knowledge, this is the first report on $\delta^{107/109}\text{Ag}$ variations in environmental samples. Significant differences in Ag isotope ratios were found among NIST SRM 978a standard, sediment CRM PACS-2, domestic sludge SRM 2781, industrial sludge 2782 and the fish liver CRM DOLT-4. The sediment CRM PACS-2 has very small negative $\delta^{107/109}\text{Ag}$ value of -0.025 ± 0.012 ‰ (2SD, n=4). The domestic sludge SRM 2781 has a negative $\delta^{107/109}\text{Ag}$ value of -0.061 ± 0.010 ‰ (2SD, n=4), whereas industrial sludge SRM 2782 has a positive $\delta^{107/109}\text{Ag}$ value of $+0.044 \pm 0.014$ ‰ (2SD, n=4), which may indicate the contribution of Ag from different anthropogenic inputs. DOLT-4 has much larger negative value of -0.284 ± 0.014 ‰ (2SD, n=4), possibly caused by biological processes. These observations confirm

that Ag isotope fractionation may provide a useful tool for fingerprinting sources of Ag in the environment and for studying a wide variety of chemical and biological processes in nature. High precision of better than $\pm 0.015\text{ ‰}$ (2SD, n=4) obtained in real sample matrices makes the present method well suited for monitoring small Ag isotope fractionation in nature.

Key words: Isotope ratios, MC-ICP-MS, Isotopic fractionation, Ag, Biological tissue, sediment, sludge.

INTRODUCTION

Silver is a well-known environmental pollutant and its environmental implications are of great concerns especially since new technologies, such as recent advances in nanotechnologies, have rapidly increased nanosilver (n-Ag) usage in consumer products¹, ranging from socks, paints, bandages, food containers and even food supplements that claim to include some form of n-Ag¹⁻². The increased release of n-Ag into the environment could pose potential toxic effects on aquatic organisms and may have an effect on the human life¹⁻², consequently Ag has been defined as a high priority toxic metal in risk assessment studies by Environment Canada under Chemical Management Plan (CMP) monitoring and surveillance program list³. On the other side, little is known about the behavior, exposure routes and fate of n-Ag after being released into the environment. As a result, there is an important need to develop new approaches for fingerprinting, tracking and understanding the sources of silver in the environment.

Isotope fractionation of non-traditional stable isotopes can be used as a valuable tool for studying the biogeochemical cycles of metals⁴. We therefore propose to use high precision of Ag isotope ratio analysis by MC-ICP-MS as a novel approach for fingerprinting sources of this element in the environment and for studying a wide variety of chemical and biological processes relating to Ag in nature. Notably, silver isotopic composition in the environment has not been studied in depth compared to other heavy metal pollutants such as Hg⁵⁻¹⁹. Only recently, Yang *et al.*²⁰ reported up to +0.83‰ level variations in ¹⁰⁷Ag/¹⁰⁹Ag ratios in several Ag fortified consumer products. Such Ag isotope variations suggested that Ag isotopic composition may be a useful tracer for studying its various chemical and biological processes in nature. However, the study of Yang *et al.*²⁰ was limited to a few Ag fortified consumer products using MC-ICP-MS detection. Therefore, applications of high precision Ag isotope determination in real

environmental samples are urgently required.

Previous studies with use of MC-ICP-MS have reported precisions of Ag isotope ratios in geological samples in a range of 0.13~2‰²¹⁻²² to 0.05‰ by Schonbachler *et al*²³⁻²⁴. The study of Yang *et al.* also achieved a similar precision of 0.05‰ for Ag fortified consumer products²⁰. However, such precision might not be enough to distinguish small fractionation of Ag isotopes in the environment. The purpose of this work was to develop a more precise and optimized method for the accurate and precise determination of Ag isotope ratios in a few typical environmental sample matrices including a biological tissue, sediment and sludge to prove the concept. In this study, mass discrimination and instrument drift are corrected for by implementation of a combination of internal normalization with Pd and standard-sample-standard bracketing, without assuming identical mass bias for Pd and Ag, similar to previous used method²⁰.

EXPERIMENTAL SECTION

Instrumentation. A Thermo Fisher Scientific Neptune (Bremen, Germany) MC-ICP-MS equipped with 9 Faraday cups and a combination of cyclonic and Scott-type spray chambers with a PFA self-aspirating nebulizer MCN50 (Elemental Scientific, Omaha, NE, USA) operating at 50 $\mu\text{l min}^{-1}$ was used for all measurements. The plug-in quartz torch with sapphire injector was fitted with a platinum guard electrode. Low resolution mode was used in this study with $R_{\text{power}(5, 95\%)} \sim 300$. Optimization of the Neptune was performed as recommended by the manufacturer; typical operating conditions are summarized in Table 1.

A quadrupole ICP-MS DRC ELAN6100 (PerkinElmer Sciex, Thornhill, Ontario, Canada) or a sector field ICP-MS Element2 from Thermo Fisher Scientific (Bremen, Germany) was used for a semi-quantitative analysis. A Digiprep Jr block heater and 50 mL volume Teflon tubes (SCP Science, Quebec, Canada) were used for evaporation of samples. A Thermo IEC

Centra CL3 (Thermo Fisher Scientific, North Carolina, USA) was used for centrifuging samples. Empty 2 mL columns (part number: AC-141-AL) and 25 mL extension funnels (part number: AC-120) were purchased from Eichrom Technologies LLC (Darien IL, USA).

Reagents and Solutions. Reagent grade nitric and hydrochloric acids (Fischer Scientific Canada, Ottawa, Ontario, Canada) were purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a quartz still. Environmental grade HF and H₂O₂ was purchased from Anachemia Science (Montreal, Quebec, Canada). High-purity (18 MΩ cm) de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). SRM 978a (Ag isotope) in AgNO₃ form was obtained from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). A 1000 µg g⁻¹ stock solution of SRM 978a Ag was prepared by its quantitative dissolution in 2 % (v/v) HNO₃ solution. A 3000 µg g⁻¹ stock solution of Pd was prepared by quantitative dissolution of high purity Pd metal (Johnson Matthey Plc) in a few mL HNO₃ and diluted with DIW. A 800 µg g⁻¹ Pd working standard solution was prepared by quantitatively dilute suitable amount of stock solution in 2 % (v/v) HNO₃. AG1-X8 anion exchange resin (100-200 mesh) and AG50W-X8 cation exchange resin (200-400 mesh) were obtained from Eichrom Technologies LLC (Darien IL, USA).

National Research Council Canada (NRCC, Ottawa, Canada) dog fish liver CRM DOLT-4 and harbour sediment CRM PACS-2 were used for Ag isotope ratio determination. Industrial sludge SRM 2782 and domestic sludge SRM 2781 were purchased from National Institute of Standards & Technology (Gaithersburg, MD, USA).

Sample digestion. Sample preparation was undertaken in a class-100 clean room. For sediment CRM PACS-2, 0.25g sub-samples were weighed into individual pre-cleaned Teflon digestion

vessels. Each 8 mL of HNO_3 , 1 mL of HF and 0.5 mL H_2O_2 were added to each vessel. Two procedure blanks were also prepared concurrently. The sealed vessels were heated in a Milestone microwave oven operated under the following conditions: 10 min at 50 °C and 500 W; 10 min at 140 °C and 500 W; 15 min at 180 °C and 600 W; and 45 min at 210 °C and 650 W. After cooling, the caps were removed and 6 mL of 5 M HCl were added to each vessel. The vessels were placed on a hot block and heated at 120 °C for 1h to avoid any AgCl precipitates in the solution under excess amount of Cl^- concentration. Then the contents were transferred into 50 mL Teflon tubes and placed on a hot block in a class-10 fume hood and heated at 120 °C until dryness. Following addition of 1 mL HCl, the contents were heated at 105 °C until dryness. The residues were redissolved in 5 mL of 5 M HCl with heating for 30 minutes at 85 °C followed by dilution with DIW to 50 mL which resulted in a final concentration of 0.5 M HCl. The solutions were sonicated for 30 minutes to ensure complete dissolution followed by centrifugation for a few minutes before loading the supernatant onto the column for matrix separation.

Fish liver CRM DOLT-4 and two sludge SRMs were prepared similarly as described above with exception of HF was not used for DOLT-4. Since both sludge SRM samples contain high concentration of Ag, 0.050 g sub-samples instead of 0.25 g were used.

Column separation. Anion exchange columns containing 1.25 mL each of AG1-X8 resin and cation exchange columns containing 1.80 mL each of AG50W-X8 resin were cleaned and preconditioned with adequate acids as detailed in Table 2. After the sample loading onto the anion columns in 0.5 M HCl, the columns were rinsed each with 5 x 10 mL 0.5 M HCl, 3 x 10 mL 0.1 M HCl followed by 3 x 5 mL of 0.001 M HCl. The rack holding anion exchange columns were then placed on the top of the other rack holding cation exchange columns (Figure 1). To elute anion exchange columns and at same time to load and elute cation exchange columns, 9 x 5

mL each 1 M HNO₃ were passed through each set of tandem column and collected into 50 mL Teflon tubes. The collected fractions were dried on a hot plate at 120 °C to dryness. The whole tandem column separation procedure was repeated one more time. The final collected total 45 mL of 1 M HNO₃ fractions were dried on a hot plate at 120 °C to dryness. The residues were redissolved in a mixture of 0.05 mL HNO₃, 0.15 mL of HCl and 0.3 mL DIW at 105°C for 30 minutes followed by dilution to 5 mL with DIW prior to MC-ICP-MS measurements. An aliquot of 0.50 mL each of these purified solutions was taken out for total semi-quantitative analysis to check left over matrix elements. The remaining purified solutions were each spiked with 0.0113 g of 800 µg g⁻¹ Pd standard solution prior to MC-ICP-MS ratio determination.

Analysis Procedure and Data Processing. Samples and standards were introduced into the plasma using self-aspiration nebulizer at 50 µL min⁻¹. Intensities of Ag and Pd isotopes obtained (shown in Table 1) from a procedure blank solution in 1 % (v/v) HNO₃ and 3 % (v/v) HCl were subtracted from all samples and standards. Samples were introduced in the sequence of SRM 978a-sample-SRM 978a. A static run was employed to collect ¹⁰⁴Pd, ¹⁰⁵Pd, ¹⁰⁷Ag and ¹⁰⁹Ag isotopes on Faraday cups at L3, L2, Central, and H2 positions, respectively. Data acquisition parameters are summarized in Table 1. Five measurements were made on each test sample solution. A bracketing standard solution of SRM 978a in 1 % (v/v) HNO₃ and 3 % (v/v) HCl was prepared for each sample so as to contain similar concentrations of Ag and Pd.

Major matrix elements and elements which could pose potential polyatomic interferences on Ag and Pd isotopes were assessed in the samples using a quadrupole ICP-MS or a sector field ICP-MS and semi-quantitative analysis mode.

RESULTS AND DISCUSSION

Optimization and mass bias correction. Good measurement precision for Ag isotope ratio was

achieved using an integration time of 4.194 s acquiring data with 10 cycles and 5 blocks within a reasonable measurement time. One measurement requires about 7 min, including uptake and washout, consuming approximately 0.35 mL of sample. In this study, a high performance skimmer cone for Neptune was used to improve sensitivity for high precision Ag isotope ratio measurements in generally low Ag contained environmental samples.

As detailed in a recent review²⁵, for accurate and precise isotope ratio determination it is essential to correct for mass discrimination observed in MC-ICP-MS. It is a common practice to use internal standard for mass bias correction of analyte isotope ratios. However, assuming identical mass bias correction factors for both analyte (e. g. Ag) and internal standard (e. g. Pd) used in previous studies²¹⁻²⁴ is both unnecessary and incorrect^{20, 25}. Thus, a mass bias correction approach based on internal normalization with Pd in combination with standard-sample-standard bracketing used previously for Ag isotope ratio determination in commercial products²⁰ was adopted here. However, the isotope pair of $^{104}\text{Pd}/^{105}\text{Pd}$ instead of $^{106}\text{Pd}/^{108}\text{Pd}$ which used previously²⁰ was chosen in this study to avoid any possible ^{106}Cd interference on ^{106}Pd and ^{108}Cd interference on ^{108}Pd due to a small amount of Cd left over in the purified sample digests after column separation. The “certified” value of 1.07638 for $^{107}\text{Ag}/^{109}\text{Ag}$ in SRM 978a was used to obtain mass bias corrected $^{104}\text{Pd}/^{105}\text{Pd}$ ratios in two adjacent standard solutions of SRM 978a and their average value was then used to calculate mass bias corrected Ag isotope ratios in the samples based on an exponential law for mass bias correction²⁶ used in the software of Neptune:

$$R_m = R_T \cdot \left(\frac{m_i}{m_j}\right)^f \quad (1)$$

where subscripts m and T indicate measured and mass bias corrected ratios, respectively; f is the mass bias correction factor; m_i and m_j are the absolute masses of the isotopes of interest.

For comparison purpose, a δ -value scale established relative to a common standard solution is used for this study.

$$\delta^{107/109}\text{Ag} = \left(\frac{R_T^{\text{sample}}}{R_T^{\text{std}}} - 1 \right) \cdot 1000 \text{‰} \quad (2)$$

where R_T^{sample} and R_T^{std} are mass bias corrected (or “true”) ratios in the sample and standard, respectively. Based on this approach, a $\delta^{107/109}\text{Ag}$ of $-0.002 \pm 0.009\text{‰}$ (mean and 2SD, $n=5$) in a 100 ng g^{-1} solution of SRM978a containing $2 \text{ }\mu\text{g g}^{-1}$ Pd was obtained, confirming accurate and precise Ag ratio determination using present mass bias correction method.

Tandem column matrix separation. In addition to instrumental mass bias, sample matrix could have large effects on accurate ratio measurements. To properly correct for these effects, separation of analyte from sample matrix is generally necessary²⁰, since in practice it is impossible to match all matrix elements between a sample and a standard solution. It is now widely recognized that non-quantitative recovery of analyte as a result of matrix separation may induce isotope fractionation²⁷⁻²⁸, and quantitative (above 95 %) recovery of analyte is thus required to ensure accurate results.

During our preliminary studies, an Ag standard solution at 500 ng g^{-1} was used to test recoveries of anion and cation exchange columns, respectively. It was found that eluting the anion exchange column with 1 M HNO_3 instead of 0.5 M HNO_3 used previously²¹⁻²⁴ significantly decreased the total volume of the acid solution needed to quantitatively elute Ag from this column. In addition, quantitative recovery of Ag from the cation exchange column was obtained when 1M HNO_3 was used for loading and elution. Thus 1M HNO_3 was used for all subsequent experiments. To improve the sample throughput of column separation and sample

preparation, a tandem column setup was applied (Figure 1), after sample loading and rinsing of the anion exchange column separately (see Table 2). This way the eluent from the anion exchange column was directly dripped into the cation exchange column for loading and eluting simultaneously. Based on a 0.25 g sub-sample for a PACS-2 digest, a 25 mL of 1M HNO₃ is enough to quantitatively elute Ag from the tandem column setup. However for samples containing higher concentration of Ag such as SRM 2781 (98±8 µg g⁻¹), a 45 mL of 1 M HNO₃ is needed for complete elution of Ag from the columns. Thus, a 45 mL of 1M HNO₃ was used in all subsequent experiments. The present tandem column separation setup allows a batch separation (usually 12 samples at a time) to be finished within two days, an improvement compared to three days required in previous studies²³⁻²⁴.

Initially, the collected 1 M HNO₃ eluent (45 mL) was used for Ag ratio determination and for TotalQuant measurements to check the efficiency of matrix separation using tandem column set up. However, a loss of Ag signal in a collected 45 mL 1 M HNO₃ was observed as this solution aged and the Ag signal completely disappeared after the solution was left stand for two weeks. This is likely due to a trace amount of Cl⁻¹ present in this solution from the 0.001 M HCl used for rinsing of anion exchange column and thus precipitates Ag out from the solution with time. To overcome this, the collected Ag fraction in 45 mL of 1 M HNO₃ was heated to dryness at 120 °C. The residues were then redissolved in a mixture of 0.05 mL HNO₃, 0.15 mL of HCl and 0.3 mL DIW at 85 °C for 30 minutes, followed by dilution to 5 mL with DIW resulting in 1 % (v/v) HNO₃ and 3 % (v/v) HCl solution. Under this these conditions, the Ag concentration was found to be very stable.

Spike recovery tests were conducted on PACS-2 digests with a 2 µg Ag spike and quantitative recovery of 99.8±2 % (2SD, n=4) of Ag was obtained. Washing the columns prior to

use ensured that the overall column separation procedural blank was less than 0.3 ng Ag (absolute), about 200-fold less than the absolute amount of Ag in the processed sub-samples. However, intensities for Ag and Pd isotopes in all samples were procedure blank corrected in order to achieve the best results. Processing a 100 ng g⁻¹ NIST 987a Ag standard through the columns did not induce any detectable mass fractionation of Ag ratio in the purified solutions, ($\delta^{107/109}\text{Ag}$ value of $-0.001 \pm 0.010\%$, mean and 2SD, n=4), as would be expected when quantitative recovery is achieved.

Matrix effects. Initially, semi-quantitative analysis of purified digests using single tandem column separation was performed to assess the efficiency of matrix separation of the columns. Although concentrations of matrix elements were significantly reduced, some matrix elements were still detected at levels of greater than 0.002, a ratio of individual matrix element concentration to Ag concentration, in the purified digests (Table 3). Clearly, highest ratios of matrix element concentrations to Ag concentration were found in PACS-2 digests purified using a single run. This was expected since total loading of sediment PACS-2 was the highest with use of a sub-sample size of 0.25 g compared to 0.050 g of SRM 2781 or SRM 2782.

Previous studies on matrix effects of Na, K, Sn and W²⁰ revealed that there is no need to match matrix elements and analyte perfectly in the sample and standard due to small effects on the $\delta^{107/109}\text{Ag}$ value. As reported previously²⁰, a $\delta^{107/109}\text{Ag}$ value of $0.93 \pm 0.08 \%$ (mean and 2SD, n=10) obtained in a 100 ng g⁻¹ solution of SRM 978a spiked with 5000 ng g⁻¹ each of Na and K against a pure solution of SRM 978a using direct standard-sample-standard mass bias correction, reduced to a value of $0.09 \pm 0.04 \%$ (mean and 2SD, n=10) with use of combination mass bias correction of standard-sample-standard bracketing and Pd internal normalization. This observation suggests that although the mass bias for Ag and Pd is not identical, but they behave

in a very similar manner, and matrix effects on $\delta^{107/109}\text{Ag}$ value are significantly reduced when internal normalization with Pd in combination with standard-sample-standard bracketing for mass bias correction is used. Therefore, a Pd at high concentration ($2\ \mu\text{g g}^{-1}$) was added to both purified digests and Ag standards for Ag isotope ratio measurements, which was not only used as an internal standard but also as a common doping matrix to reduce matrix effects of any impurities present in the purified digests. Similar approach was reported by Barling and Weis²⁹ wherein Mg was successfully used as common doping matrix for accurate and precise Pb isotope ratio measurements.

The effect of impurities in the purified sample digest on Ag isotope ratios measurement was investigated by analyzing $100\ \text{ng g}^{-1}$ standard solution of Ag prepared from SRM 978a in the presence of 2.5 and 5-fold of matrix elements found in digests. Compared to a pure solution of SRM 978a and using $2\ \mu\text{g g}^{-1}$ Pd as internal standard in combination with standard-sample-standard bracketing for mass bias correction, $\delta^{107/109}\text{Ag}$ values were not significantly affected by the spiked matrix elements (Table 4). This confirms that accurate Ag isotope ratio results should be obtained using a single tandem column matrix separation. However, the $\delta^{107/109}\text{Ag}$ values obtained in single tandem column purified PACS-2 digests, varied from -0.17 to -0.67 ‰ for five PACS-2 sub-samples. This observation suggests that other unidentified matrix impurities, most likely the organic matrix or some anions which had poor detection by ICP-MS such as S, Br, I were present in the single tandem column purified PACS-2 digests, which affected the observed variability in $\delta^{107/109}\text{Ag}$ values.

Therefore, multiple tandem column matrix separations were investigated in subsequent experiments for further purification of sample matrix in order to obtain accurate and precise Ag isotope ratio results. As shown in Table 4, a precise $\delta^{107/109}\text{Ag}$ value of $-0.025 \pm 0.014\text{‰}$ (2SD,

n=4) was obtained for double purified PACS-2 digests. No significant difference in $\delta^{107/109}\text{Ag}$ values was obtained in triple purified PACS-2 digests, confirming double tandem column separations sufficiently removed sample matrix (Table 5). However, triple tandem column separations may be needed for samples containing higher matrix elements or larger sample size used. Similarly, no differences in $\delta^{107/109}\text{Ag}$ values were detected in DOLT-4 and SRM 2781 digests purified using double or triple tandem column separations. Thus, double tandem column matrix separations were used in all subsequent experiments.

Potential spectral interferences from $^{91}\text{Zr}^{16}\text{O}^+$, $^{90}\text{Zr}^{16}\text{OH}^+$, $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$, $^{92}\text{Mo}^{16}\text{OH}^+$, $^{104}\text{Ru}^+$, $^{90}\text{Zr}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{O}^+$, and $^{91}\text{Zr}^{16}\text{OH}^+$ on both Ag isotopes and ^{104}Pd and ^{105}Pd could occur in samples containing these elements and thus could degrade the accuracy of final results and should be eliminated. Semi-quantitative analysis of all purified sample solutions revealed that concentrations of Zr and Mo were less than 0.01 ng g^{-1} compared to Ag concentrations of $50\text{--}490 \text{ ng g}^{-1}$, confirming insignificant interferences of their oxides and hydroxides. Ru was found to be less than 0.005 ng g^{-1} in the purified sample solutions, confirming interference free on ^{104}Pd . In addition, no significant amount of Pd (less than 0.005 ng g^{-1}) was found in the purified digests. These observations confirm that followed by double tandem column matrix separation, accurate determination of Ag isotope ratios can be obtained by using the $^{104}\text{Pd}/^{105}\text{Pd}$ isotope pair for a combination of internal normalization and standard-sample-standard bracketing for mass bias via MC-ICP-MS detection.

Validation of the method and final results. To validate the proposed method, four replicate solutions of SRM 978a at 100 ng g^{-1} Ag were subjected to column separation and sample preparation processes. A value of $-0.003 \pm 0.010\text{‰}$ for $\delta^{107/109}\text{Ag}$ (2SD, n=4) was obtained, confirming accurate results can be obtained using the proposed method.

For the final determination of Ag isotope ratios in environmental samples, four replicate test samples were prepared and each was measured 5 times under the optimized experimental conditions. Results are presented in Table 5. Amongst the environmental samples examined, significant differences in Ag isotope ratios were found among NIST SRM 978a standard, sediment CRM PACS-2, domestic sludge SRM 2781, industrial sludge SRM 2782 and DOLT-4. A negative $\delta^{107/109}\text{Ag}$ value of -0.284 ± 0.014 ‰ (2SD, n=4) was obtained in DOLT-4, a dog fish liver. This observed Ag isotope fractionation may be caused by enrichment of the heavy ^{109}Ag isotope during elimination processes from the liver. A negative $\delta^{107/109}\text{Ag}$ value of -0.061 ± 0.010 ‰ (2SD, n=4), was obtained in the domestic sludge SRM 2781 which is a sample from the Metropolitan Denver Sewage District No.1 site³⁰. This may indicate the contribution of Ag from anthropogenic input from consumer products. For an example, a negative $\delta^{107/109}\text{Ag}$ value of -0.08 ± 0.05 ‰, (2SD, n=4) measured previously by Yang *et al.*²⁰ in highly fortified Ag containing X-static socks. The released Ag from these products into domestic sludge could result in a negative $\delta^{107/109}\text{Ag}$ value in such material. Interestingly, a slightly positive $\delta^{107/109}\text{Ag}$ value of $+0.044 \pm 0.014$ ‰ (2SD, n=4) was obtained in the industrial sludge SRM 2782 which was obtained from an industrial site in northern New Jersey involved in pharmaceutical research as effluence, according to the SRM certificate³¹. This observation suggests a different type of anthropogenic input of Ag for industrial use, such as n-Ag. For an example, a colloidal Ag dietary supplement measured previously by Yang *et al.*²⁰ has a positive $\delta^{107/109}\text{Ag}$ value of $+0.83 \pm 0.06$ ‰ (2SD, n=4). The released Ag from manufacturers of producing this supplement into industrial sludge could result in a positive $\delta^{107/109}\text{Ag}$ value in such material. A very small negative $\delta^{107/109}\text{Ag}$ value of -0.025 ± 0.012 ‰ (2SD, n=4) was obtained for PACS-2, a marine

sediment CRM collected from Esquimalt harbor, B. C., Canada, may be a result of a combination of industrial waste water inputs and natural sources.

A 3.3-fold improvement in precision of $\delta^{107/109}\text{Ag}$ values of better than $\pm 0.015\text{‰}$ (2SD, $n=4$) was obtained in all sample matrices compared to that obtained previously²⁰⁻²⁴, due to an improved sensitivity with use of high performance cone on the MC-ICP-MS Neptune, makes the present method well suited for the high precision determination of very small Ag fractionations in nature.

CONCLUSION

An accurate and precise method has been developed for the determination of Ag isotope ratios in environmental samples by MC-ICP-MS. Mass discrimination and instrument drift were corrected by a combination of internal normalization with Pd and standard-sample-standard bracketing, without assuming identical mass bias for Pd and Ag. Efficient purification of Ag from sample matrices was obtained by a two stage tandem column setup with use of anion and cation exchange resin, subsequently. High precision of better than $\pm 0.015\text{‰}$ (2SD, $n=4$) obtained in real sample matrices makes the present method suitable for monitoring small degrees (e.g. less than 0.1 ‰ of $\delta^{107/109}\text{Ag}$) of Ag isotope fractionation that may be found in nature.

To the best of our knowledge, this is first report on $\delta^{107/109}\text{Ag}$ values in environmental samples. Significant differences in Ag isotope ratios were found among NIST SRM 978a standard, sediment CRM PACS-2, domestic sludge SRM 2781, industrial sludge SRM 2782 and DOLT-4. These observations further confirm that such data may provide a useful tool for fingerprinting sources of Ag in the environment and for studying a wide variety of chemical and biological processes in nature. Future studies will be aimed at the determination of Ag isotope

fractionations in samples collected from a well defined nature environment where effluents from wastewater treatment plant, waters, sediments and biological samples such as fishes can be collected.

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Table 1. MC-ICP-MS operating conditions

Instrument settings	
Rf power	1250 W
Plasma Ar gas flow rate	15.0 L min ⁻¹
Auxiliary Ar gas flow rate	1.00 L min ⁻¹
Ar carrier gas flow rate	1.087 L min ⁻¹
Sampler cone (nickel)	1.1 mm
Skimmer cone (H, nickel)	0.8 mm
Lens settings	Optimized for maximum analyte signal intensity
Data acquisition parameters	
Scan type	Static measurements
Cup configuration	(¹⁰⁴ Pd)L3, (¹⁰⁵ Pd)L2, (¹⁰⁷ Ag)C and (¹⁰⁹ Ag)H2
Resolution	~300
Sensitivity	43 V/ppm for ¹⁰⁷ Ag
Blank 1% (v/v) HNO ₃ and 3%HCl	0.0016 V for ¹⁰⁷ Ag, 0.0015 V for ¹⁰⁹ Ag, 0.005 V for ¹⁰⁴ Pd and 0.011 V for ¹⁰⁵ Pd
Integration time	4.194 s
Number of Integrations	1
Cycles/Blocks	10/5

Table 2. Column separation procedure.

Anion exchange column AG1-X8	Step
3x10 mL 2 M HCl	Clean
3x5 mL 0.5 M HCl	Condition
Sample in 50 mL 0.5 M HCl	Load
5x10 mL 0.5 M HCl	Rinse
3x10 mL 0.1 M HCl	Rinse
3x5 mL 0.001 M HCl	Rinse
9x5 mL 1 M HNO ₃	Elute*
Cation exchange column AG50W-X8	
3x10 mL 6 M HNO ₃	Clean
3x10 mL 1 M HNO ₃	Condition
9x5 mL 1 M HNO ₃	Load +Elute*
* tandem column setup	

Table 3. Semi quantitative results for matrix elements in purified sample digests, ratio of individual matrix element concentration to Ag concentration in the digests.

Analyte	DOLT-4 (46.5 ng g ⁻¹ Ag in purified sample solution)		PACS-2 (60 ng g ⁻¹ Ag in purified sample solution)		SRM 2781 (490 ng g ⁻¹ Ag in purified sample solution)		SRM 2782 (153 ng g ⁻¹ Ag in purified sample solution)	
	Once	Twice	Once	Twice	Once	Twice	Once	Twice
# of column separation								
Na	0.08	0.04	0.40	0.03	0.02	0.002	0.02	0.01
Mg	0.03	0.01	1.9	0.01	0.01	<0.002	0.006	0.003
Al	0.05	0.04	8.5	0.008	<0.002	<0.002	0.004	0.002
K	0.09	<0.02	3.1	<0.02	0.02	<0.005	<0.002	<0.002
Ca	<0.002	<0.002	4.5	<0.02	0.1	<0.005	<0.002	<0.002
Ti	<0.005	<0.005	0.02	<0.01	<0.005	<0.005	<0.005	<0.005
Zn	0.05	<0.002	0.02	0.02	0.01	<0.002	0.009	<0.002
Cd	0.22	0.10	0.32	0.10	0.02	0.006	0.024	0.007
Sb	<0.002	<0.002	0.04	<0.002	0.01	<0.002	<0.002	<0.002
Sn	0.15	0.01	0.28	0.05	0.13	0.02	0.29	0.07
Ba	0.003	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Bi	0.01	0.002	0.01	0.01	0.05	0.04	0.04	0.03
Nb	<0.002	<0.002	<0.002	<0.002	0.01	<0.002	0.002	<0.002
W	0.03	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Tl	0.02	<0.002	0.12	0.06	<0.002	<0.002	0.003	<0.002
Pb	0.04	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
U	0.01	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

Only ratios of matrix element concentration to Ag concentration were greater than 0.002 are reported.

Table 4. Results for Matrix Effects.

Element	Matrix elements concentrations, ng g ⁻¹ (ratio of matrix element concentration to Ag concentration)			
	100 ppb Ag SRM 978a, spiked with 5 times of matrix elements found in digest	100 ppb Ag SRM 978a, spiked with 2.5 times of matrix elements found in digest	PACS-2 (60 ng g ⁻¹ Ag) matrix element concentrations found in purified once PACS-2 digest	PACS-2 (60 ng g ⁻¹ Ag) matrix element concentrations found in purified twice PACS-2 digest
Na	250 (2.5)	125 (1.25)	25 (0.40)	1.8 (0.02)
Mg	1460 (14.6)	730 (7.3)	115 (1.9)	0.6 (0.01)
Al	4250 (42.5)	2125 (21.25)	510 (8.5)	0.5 (0.008)
K	1750 (17.5)	875 (8.75)	180 (3.1)	<1 (<0.02)
Ca	2250 (22.5)	1125 (11.25)	270 (4.5)	<1 (<0.02)
Ti	50 (0.5)	25 (0.25)	1(0.02)	<0.5 (<0.01)
Zn	100 (1.0)	50 (0.5)	1.2 (0.02)	1.2 (0.02)
Cd	160 (1.6)	80 (0.8)	16 (0.32)	6 (0.10)
Sb	20 (0.2)	10 (0.1)	2.4 (0.04)	<0.1(<0.002)
Sn	140 (1.4)	70 (0.7)	17 (0.28)	3 (0.05)
Ba	2 (0.02)	1 (0.01)	<0.1(<0.002)	<0.1 (<0.002)
Bi	25 (0.25)	12.5 (0.125)	0.6 (0.01)	0.6 (0.01)
Nb	5 (0.05)	2.5 (0.025)	<0.1 (<0.002)	<0.1 (<0.002)
W	15 (0.15)	7.5 (0.075)	<0.1 (<0.002)	0.4
Tl	60 (0.6)	30 (0.3)	7 (0.12)	7 (0.06)
Pb	20 (0.2)	10 (0.1)	<0.1 (<0.002)	<0.1 (<0.002)
U	5 (0.05)	2.5 (0.025)	<0.1 (<0.002)	<0.1 (<0.002)
Measured $\delta^{107/109}\text{Ag}$ against pure SRM 978a standard, mean and 2SD, n=5				
$\delta^{107/109}\text{Ag}$	-0.003±0.010‰	-0.009±0.010‰	-0.35±0.44‰	-0.025±0.012‰

Table 5. Ag isotope ratio results in environmental samples

Sample ID	$\delta^{107/109}\text{Ag}$ (‰) (2SD, n=4)	
# of column separation	Twice	Three times
DOLT-4, Dogfish liver	-0.284±0.014	-0.284±0.014
PACS-2, sediment	-0.025±0.014	-0.025±0.010
SRM 2781, domestic sludge	-0.061±0.010	-0.062±0.008
SRM 2782, industrial sludge	+0.044±0.014	NA

Figures and Captions

Figure 1: Tandem column setup.

Figure 1: Tandem column setup.