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On-line determination of silver in sea-water and marine sediment by inductively coupled plasma mass spectrometry

Lu Yang* and Ralph E. Sturgeon

Institute for National Measurement Standards, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. E-mail: Lu.Yang@nrc.ca

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An on-line flow injection method for the direct determination of silver in sea-water using isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) is described. A mini-column packed with 50 μl Dowex 1-X8 anion exchange resin was used to separate and concentrate Ag from sea-water following on-line merging with 0.5 M HCl. Recoveries of $100 \pm 1\%$ and $96 \pm 1\%$ were obtained for NRC CRMs SLEW-3 and CASS-4, respectively. One run can be completed in less than 6 min using a 12 ml volume of sea-water. The detection limit (3σ), estimated at 0.06 pg ml^{-1} , is superior to previously published methods. Dissolved Ag concentrations of 1.93 ± 0.10 , 5.15 ± 0.10 and $5.42 \pm 0.10 \text{ pg ml}^{-1}$ were obtained in SLEW-3, CASS-2 and CASS-4 CRMs, respectively. The method was also assessed for determination of Ag in a marine sediment CRM MESS-3, and a concentration of $0.169 \pm 0.002 \text{ } \mu\text{g g}^{-1}$ was obtained using ID ICP-MS after an off-line column separation, in agreement with the certified value of $0.18 \pm 0.02 \text{ } \mu\text{g g}^{-1}$. The on-line method was also applied to analyses of sea-water and sufficiently diluted digests of marine sediments using an external calibration technique. Concentrations of $1.96 \pm 0.10 \text{ pg ml}^{-1}$ (mean and one standard deviation, $n = 3$) and 5.55 ± 0.15 ($n = 3$) pg ml^{-1} were obtained for dissolved Ag in SLEW-3 and CASS-4, respectively, in agreement with results generated by ID ICP-MS. A concentration of 0.181 ± 0.004 ($n = 3$) $\text{ } \mu\text{g g}^{-1}$ in MESS-3 was obtained, based on 200-fold diluted digests, in agreement with the certified value.

Introduction

The high concentration of dissolved solids (3.5% by weight) and typically less than ng ml^{-1} concentrations of trace metals, make sea-water one of the most challenging samples for analytical chemists. Over the past decade, clean sampling techniques developed by researchers such as Bruland *et al.*¹ have been combined with modern developments in sensitive instrumentation to make reliable trace metal determinations possible in sea-water. The interest in measuring silver in natural waters has increased due to concerns over its toxicity to aquatic organisms.²⁻⁴ Currently, few reports addressing the determination of Ag in sea-water exist. Commonly used techniques for Ag determination often involve some form of pre-concentration, including flotation,⁵ organic extraction^{3,4,6,7} or sorption on columns⁸ followed by quantitation using atomic absorption spectrometry, although several direct approaches have also been developed. An organic extraction method based on complexation with ammonium 1-pyrrolidine dithiocarbamate and diethylammonium diethyldithiocarbamate (APDC-DDDC) and extraction of Ag from a few hundred ml volume of sea-water utilised graphite furnace atomic absorption spectrometry (GFAAS) for detection.^{3,4,6} An average detection limit of 0.4 pg ml^{-1} was achieved. Bermejo-Barrera *et al.*⁹ undertook the direct determination of Ag in sea-water using GFAAS, reporting a detection limit of $0.5\text{--}1.1 \text{ ng ml}^{-1}$ based on a 20 μl injection volume. Gornushkin *et al.*¹⁰ achieved a detection limit of 9 pg ml^{-1} for Ag determination in sea-water by laser excited atomic fluorescence spectrometry in combination with electrothermal atomization. Recently, Shpigun and Kopytova¹¹ obtained a 5 pg ml^{-1} detection limit for Ag determination in sea-water based on anodic stripping voltammetry.

The natural concentration of Ag in sea-water²⁻⁴ is typically no more than a few pg ml^{-1} . It is obvious that, for accurate determination of these ultra-trace levels of Ag in such a complex matrix, highly sensitive and selective methods of

analysis are required. Inductively coupled plasma mass spectrometry (ICP-MS) has been used for the determination of trace elements in a variety of sample matrices because of its high sensitivity, large linear range and multi-element capability. Furthermore, if two interference free isotopes of a given element can be found, isotope dilution ICP-MS (ID-ICP-MS) generally provides better accuracy and precision than other calibration techniques, such as external calibration, because a ratio, rather than an absolute intensity measurement, is used for quantitation of the analyte concentration.¹²⁻¹⁴ Once isotopic equilibration is achieved, ID-ICP-MS is theoretically capable of compensating for any loss of analyte during sample preparation, suppression of ion sensitivities by concomitant elements in the sample matrix and instrument drift. However, samples having high dissolved solid content (*e.g.*, sea-water) are still, for preference, not analyzed directly by ICP-MS because blockage of the cones and deposition of the sample matrix on ion lenses may degrade analytical results. Furthermore, polyatomic interferences arising from the sea-water matrix must be controlled in order to ensure accurate results. Simple dilution of sea-water prior to ICP-MS analysis can minimize the former effects to some extent, but this approach was avoided in this study due to the already very low concentration of Ag (a few pg ml^{-1}) in sea-water. Polyatomic interferences observed with quadrupole ICP-MS can also be overcome to some degree by using high resolution ICP-MS or reaction cell technology. Unfortunately, potential interferences from $^{91}\text{Zr}^{16}\text{O}^+$, $^{90}\text{Zr}^{16}\text{OH}^+$, $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$, $^{92}\text{Mo}^{16}\text{OH}^+$ on both Ag isotopes cannot be resolved on present HR ICP-MS instrumentation (at 10000 resolution). Alternatively, a chemical separation and concentration of the analyte from the matrix may provide a flexible and economical approach. This not only significantly reduces any polyatomic interferences on the analyte, but also substantially improves the method's detection limit and therefore results in potentially more accurate results by ICP-MS analysis.

The goal of this study was to develop a simple and rapid on-line method having sufficient detection power for determination of Ag in sea-water using isotope dilution ICP-MS. A mini-column packed with Dowex 1-X8 strong base anion exchange resin, having a styrene divinylbenzene co-polymer backbone and tertiary ammonium as the function group was selected for use to separate and concentrate Ag. The developed method was subsequently applied to determine Ag in a marine sediment Certified Reference Material (NRCC MESS-3) having significant Zr, Mo and Nb content. Whereas both Ag isotopes are prone to polyatomic interferences ($^{91}\text{Zr}^{16}\text{O}^+$ and $^{90}\text{Zr}^{16}\text{OH}^+$ on $^{107}\text{Ag}^+$ and $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$ and $^{92}\text{Mo}^{16}\text{OH}^+$ on $^{109}\text{Ag}^+$) when Ag is directly determined in the sediment digests by ICP-MS, the technique described alleviated these problems.

Experimental

ICP-MS system

All measurements were made with a PerkinElmer SCIEX (Concord, Ontario, Canada) ELAN 6000 ICP-MS equipped with a Gem cross-flow nebulizer. A quartz torch with an alumina sample injector tube was used. The double-pass Rytan spray chamber was mounted outside the torch box and maintained at room temperature. The ICP-MS was optimized daily for nebulizer gas flow, lens voltage and rf power according to manufacturer's recommendations. Typical operating conditions used for measuring $\text{Ag}^{107}/\text{Ag}^{109}$ ratios are given in Table 1.

Flow injection system. A PerkinElmer (Norwalk, CT, USA) FIAS-400 MS flow injection accessory was used for on-line column separation and concentration. A schematic diagram of the flow injection system during the pre-fill step is shown in Fig. 1. The resin was packed into a PerkinElmer column (Part No. B050-7950, 10 mm length, 3 mm id, 50 μl capacity). The

Table 1 ICP-MS operating conditions

Rf power	1050 W
Plasma Ar gas flow rate	15.0 l min^{-1}
Auxiliary Ar gas flow rate	1.0 l min^{-1}
Nebulizer Ar gas flow rate	0.700 l min^{-1}
Sampler cone (nickel)	1.00 mm aperture
Skimmer cone (nickel)	0.88 mm aperture
Lens voltage	7.50 V
Scanning mode	Peak hopping
Points per peak	1
Dwell time	50 ms
Sweeps per reading	1
Readings per replicate	700
Number of replicates	1

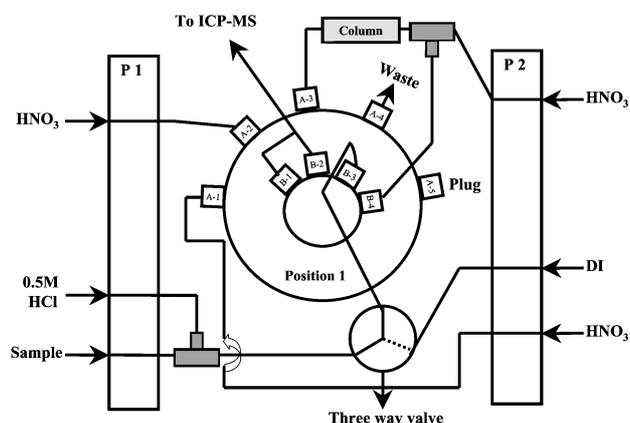


Fig. 1 Schematic diagram of FIAS-400 flow injection system.

column holder was a metal free Global FIA (Part No. MC-CH-1, Gig Harbor, WA, USA) threaded sleeve. Tygon pump tubings were used to deliver sample and reagents: 1.14 mm id for the samples and HNO_3 acid lines, 1.52 mm id for the deionized water (DIW) and 0.76 mm id for the 0.5 M HCl. All connections and tees were 0.25–28 low pressure Tefzel flangeless fittings (Upchurch Scientific Inc., Oak Harbor, WA, USA) and 1.58 mm od PTFE tubing (Cole-Parmer, Chicago, IL, USA). A three-way solenoid valve (Cole Parmer, Part No. P-98300-02) was activated by a home-made 12 V dc power supply which was controlled by the remote switches on the FIAS 400.

Microwave oven. A CEM MDS-2100 microwave oven (CEM Corp., Matthews, NC, USA) was used for closed vessel high pressure sample dissolution of sediment CRM MESS-3.

Reagents and solutions

Hydrochloric and nitric acids were purified by sub-boiling distillation of reagent grade feedstocks in a quartz still prior to use. Environmental grade HF was purchased from Anachemia Science (Montreal, Quebec, Canada). Deionized water (DIW) was obtained from a Nanopure ion exchange reverse osmosis system (Barnstead/Thermolyne, Boston, MA, USA). A 1000 $\mu\text{g ml}^{-1}$ stock solution of Ag was prepared by dissolution of the high purity metal (Johnson, Matthey & Co. Ltd., London, UK) in HNO_3 . Working standards, which were used for the ^{109}Ag reverse spike isotope dilution check, were prepared by serial dilution of the stock with DIW containing 1% HNO_3 . The resin used for column separation and concentration was 200–400 mesh Dowex 1-X8 anion exchange resin (Bio-Rad Laboratories, Richmond, CA, USA).

Enriched ^{109}Ag isotope was purchased from Isotec Inc. (Miamisburg, OH, USA) as metal. A ^{109}Ag stock solution of approximately 297 $\mu\text{g ml}^{-1}$ was prepared by dissolution of an accurately weighed quantity of this metal in HNO_3 . The concentration of ^{109}Ag spike was verified by reverse spike isotope dilution.

A suite of CRMs (estuarine sea-water CRM SLEW-3, sea-water CRM CASS-2 and CASS-4 and sediment CRM MESS-3) used as test samples for method development, were obtained from Chemical Metrology, Institute for National Measurement Standards, National Research Council Canada (Ottawa, Ontario, Canada).

Procedure

Sea-water analysis. Sea-water samples were prepared in a class-10 clean environment. Aliquots of 500 ml volumes of SLEW-3, CASS-2 and CASS-4 sea-water were each spiked with a suitable amount of ^{109}Ag enriched isotope standard solution (resulting in a ratio of $^{107}\text{Ag}/^{109}\text{Ag}$ near 0.5 for the final solution). Three sample blanks (500 ml each) were prepared from DIW and high purity nitric acid to give a pH 1.6 solution. An identical amount of ^{109}Ag enriched isotope standard as used in the samples was added to each blank. Blanks and samples were then analyzed using on-line FIAS400 flow injection column separation and concentration with ICP-MS detection. Raw data were processed off-line using in-house software, which yielded both peak height and area. Peak area was used to generate $^{107}\text{Ag}/^{109}\text{Ag}$ ratios subsequently used to quantitate Ag concentration.

The sequence for the flow injection system is presented in Table 2. The sample was mixed on-line with 0.5 M HCl. Step 1 flushed the sample tubing leading up to the valve with new sample solution. In step 2, the main valve was switched to the #2 position and HCl adjusted sample was passed through the column (4.0 ml min^{-1}). Following sample loading, the column

Table 2 FIAS-400 program

Step	Time/s	Pump 1/rpm	Pump 2/rpm	Valve position	Solenoid valve	Function
1	30	50	0	1		Pre-fill
2	180	80	0	2		Load
3	60	0	50	2	On	Rinse
4	70	0	50	1	On	Elute
5	15	50	0	2	On	Re-condition

was washed with DIW (4 ml min^{-1}) to remove the salt residue. In step 4, 1.5 M nitric acid was pumped through the column in the reverse direction (2 ml min^{-1}) and the sequestered Ag was eluted into the plasma for measurement. Finally, the valve was returned to the wash position to return the column to a neutral pH in preparation for loading of the next sample. Samples of pH 1.6 DIW were processed through at least 5 cycles (for cleaning the entire on-line flow injection ICP-MS system) before processing the real samples. The volume of sample and blank processed each time was 12 ml under the chosen experimental conditions.

Sediment analysis. Sample preparation was conducted in a class-10 or class-100 clean environment. Six 0.25 g subsamples of MESS-3 sediment were weighed into 50 ml pre-cleaned Teflon digestion vessels. A suitable amount of ^{109}Ag enriched isotope solution (resulting in a ratio of $^{107}\text{Ag}/^{109}\text{Ag}$ near 0.5 in the final solution) was then added to each vessel. Three sample blanks (spiked with 10% of the amount of enriched isotope solution used in the samples) were processed along with the samples. After 5 ml of nitric acid and 1 ml HF had been added, the vessels were sealed and heated in a CEM MDS-2100 microwave oven with maximum power of 950 W. The heating conditions were: 10 min at a pressure of 20 psi and 80% power, 10 min at 40 psi and 80% power, 10 min at 80 psi and 80% power, 15 min at 100 psi and 80% power, 25 min at 120 psi and 80% power. After cooling, the caps were removed and rinsed. The vessels were then placed on a hot plate in a class-10 fume hood and the contents were evaporated to near dryness. The final residues were dissolved in 0.5 ml HNO_3 and then diluted to 25 ml with DIW. Digests were stored in pre-cleaned polyethylene screw-capped bottles prior to ICP-MS analysis.

In order to avoid possible contamination arising from running sediment digests on the FIAS400 ICP-MS on-line system, MESS-3 digests were analyzed by ICP-MS after an off-line column separation. The off-line column set-up was identical to the on-line system but consisted of three Tygon tube lines fitted on a Gilson peristaltic pump serving as lines 1, 2 and 3 (Fig. 1). An identical column packed with 50 μl Dowex 1-X8 resin was connected to line 1 (1.14 mm id). Two other Tygon tubes having 1.14 mm id and 0.76 mm id were used as line 2 (for sample) and line 3 (for 0.5 M HCl), respectively. The sequence of operations used with this off-line column separation was as follows. All three lines were first cleaned by pumping 1.5 M HNO_3 solution for 10 min at 2.0 ml min^{-1} and then DIW for 2 min. After placing the line 3 tubing into 0.5 M HCl solution and line 2 tubing into 10 ml of 10-fold diluted MESS-3 digest, effluents from both lines were collected in a clean bottle until line 2 was run dry. The HCl adjusted sample was then pumped through line 1 and loaded onto the column. Finally, after 2 min rinsing with DIW, the column was eluted with 1.5 M HNO_3 for 2 min and the 4 ml collected in pre-cleaned screw-capped polyethylene bottles. The eluents were then analyzed by ICP-MS to determine the $^{107}\text{Ag}/^{109}\text{Ag}$ ratios.

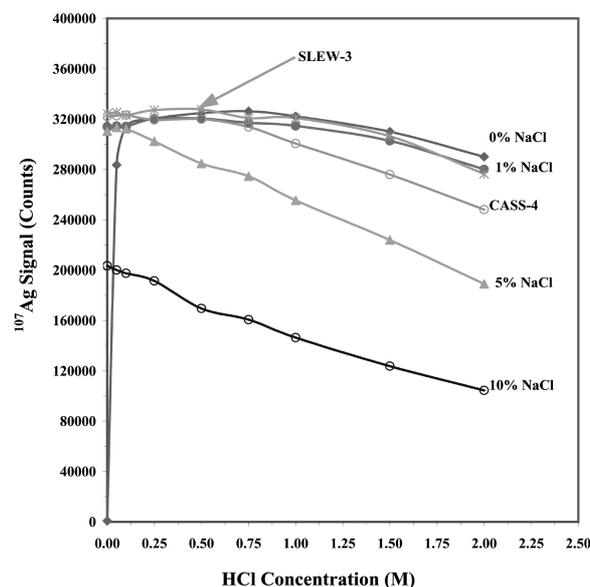
Results and discussion

Optimization

Dowex 1-X8 resin has been successfully used to separate and concentrate gold and platinum group metals from geological

samples in chloride media.¹⁵ Dissolved Ag exists mainly as chloride complexes (AgCl_2^- and AgCl_3^{2-}) in sea-water¹⁶ and should also be retained on an anion exchange resin such as Dowex 1-X8. A series of experiments was designed to investigate optimum conditions for Ag recovery using this column. The effects of HCl concentration (used for on-line adjustment), eluent strength (HNO_3 concentration), DIW rinse time, sample loading time and loading speed were investigated.

The effect of HCl concentration was clearly demonstrated by the following experiment. Six solutions were spiked with 0.1 ng ml^{-1} Ag, including pH 1.6 DIW (0% NaCl), 1% NaCl, 5% NaCl, 10% NaCl, SLEW-3 and CASS-4. All were processed using the on-line FIAS400 ICP-MS system and adjusted with HCl concentrations ranging from 0 to 2.00 M. The response from Ag (peak area of ^{107}Ag) versus HCl concentration is presented in Fig. 2. The symbols used to illustrate data points were larger than the error bars associated with replicate measurements (0.5–1.2% in precision). This was also the case for all subsequent figures. The high and constant response from 0.1 ng ml^{-1} Ag was obtained for pH 1.6 DIW solution at HCl concentrations ranging from 0.25 to 1.00 M. Sensitivity decreased at lower or higher HCl concentrations. A similar trend was noted for the 1% NaCl solution, although the optimum HCl concentration range was only 0.25–0.75 M. High and constant response from 0.1 ng ml^{-1} Ag in SLEW-3, CASS-4 and 5% NaCl solutions were observed at HCl concentrations ranging from 0 to 0.75 M, 0 to 0.50 M and 0 to 0.25 M, respectively. Sensitivity decreased at higher HCl concentrations. A continuous decrease in Ag response in 10% NaCl solution was obtained as the HCl concentration was increased from 0 to 2.00 M. Maximum Ag response in SLEW-3, CASS-4 and 5% NaCl solutions was obtained even using DIW as the on-line carrier, confirming that it is the Cl^- anion concentration that controls recovery of Ag on this Dowex 1-X8 column. This effect is clearly demonstrated in Fig. 3, where the abscissa reflects the total Cl^- concentration arising from the sample and

**Fig. 2** Effect of HCl concentration on Ag response.

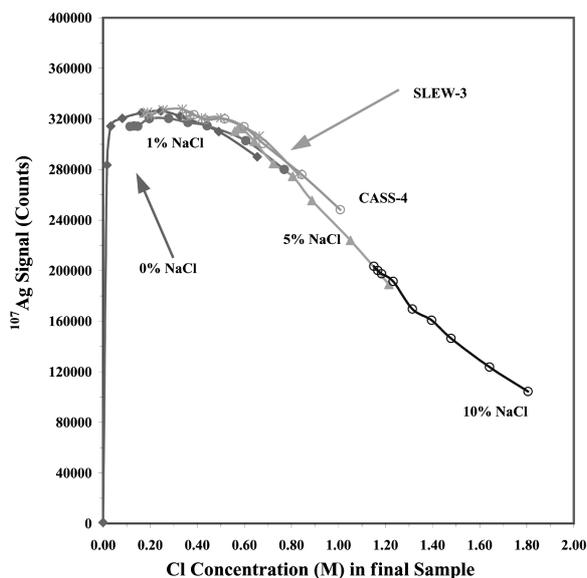


Fig. 3 Ag response versus total Cl^- concentration in the final samples.

HCl combined. Salinities of 1.5% and 3.07% for SLEW-3 and CASS-4 sea-water, respectively, were used to calculate the total Cl^- concentration. A single curve could be used to describe all results. Highest efficiency for retention of Ag on the anion exchange column was realized in the Cl^- concentration range 0.05–0.50 M in the final mixed samples. Retention efficiency decreased at both lower and higher Cl^- concentrations due to incomplete formation of Ag complex at low Cl^- concentration and the competition with excess Cl^- at high concentration, respectively. Response from a 0.1 ng ml^{-1} spike of Ag was independent of sample matrix when a standard solution or sea-water matrix was used that provided the optimum Cl^- concentration range, indicating that both good separation of Ag from the sample matrix and its quantitative recovery were achieved on this column. Spike recovery studies for all six solutions using their optimum HCl concentration further confirmed this observation. The results, presented in Table 3, show quantitative recoveries of Ag from sea-water samples adjusted to their optimum HCl concentration or optimum Cl^- concentration range (0.05–0.50 M) in the final mixed samples. Since high purity HCl is easy to obtain, HCl was chosen in this study rather than NaCl for the adjustment of Cl^- concentration. Recovery of Ag from the CASS-4 sea-water spiked at a concentration of 0.1 ng ml^{-1} was found to decrease slightly, from $99 \pm 1\%$ ($n = 3$) to $96 \pm 1\%$ ($n = 3$), as the HCl concentration was increased from its optimum at 0.10 M to 0.50 M. Although the sensitivity would be slightly impaired under such conditions, this would not affect the analytical results for determination of Ag in CASS-4 since ID ICP-MS was used for quantitation. Preliminary studies found that response from 100 ng ml^{-1} Mo, Zr and Nb solution decreased when the HCl concentration increased. In order to minimize possible polyatomic interference from $^{91}\text{Zr}^{16}\text{O}^+$, $^{90}\text{Zr}^{16}\text{OH}^+$,

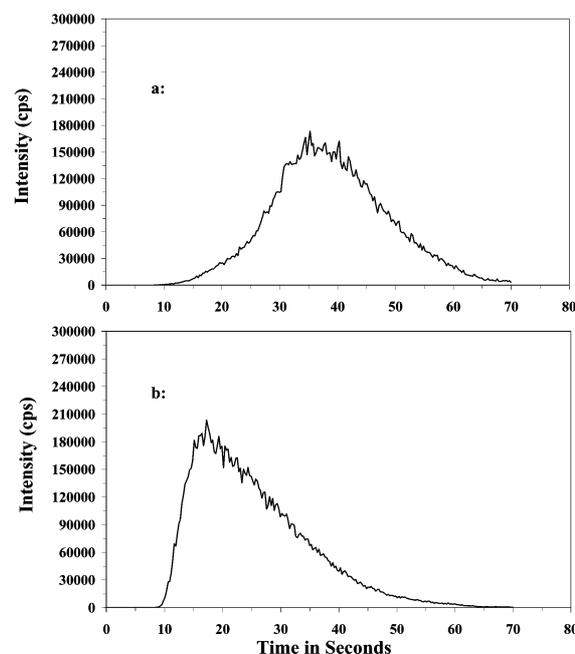


Fig. 4 Effect of HNO_3 strength on Ag retention time. a: 0.25 M HNO_3 . b: 2.0 M HNO_3 .

$^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$ and $^{92}\text{Mo}^{16}\text{OH}^+$ on both Ag isotopes, the highest HCl concentration is thus preferred. Therefore, 0.50 M HCl was chosen as the final reagent solution in order to obtain good separation as well as quantitative recovery of Ag.

The retention time for Ag in SLEW-3 (spiked at a concentration of 1.0 ng ml^{-1}) decreased from 35 to 17 s as the HNO_3 eluent was increased over a concentration range from 0.25 to 2.0 M. The intensity of the tail of the peak at the end of 70 s acquisition time dropped from 3000 to 500 cps (180000 cps at peak center), as shown in Fig. 4. The retention time only increased by 3 s using 1.5 instead of 2.0 M HNO_3 for elution, whereas the intensity of the tail of the peak at the end of 70 s acquisition time remained the same. The 1.5 M HNO_3 was chosen as eluent for further study as a result of quantitative elution of Ag from the column while incurring less damage to the cones of the ICP-MS with the more dilute acid.

The response from Ag obtained in SLEW-3 spiked at a concentration of 1.0 ng ml^{-1} did not change when the DIW rinse time was increased from 15 to 90 s. Whereas the Na^+ signal dropped 10-fold (from $8 \times 10^6 \text{ cps}$ at peak height to $7.6 \times 10^5 \text{ cps}$) when the DIW rinse time was increased from 15 to 45 s, it further decreased only 2-fold (to $3.6 \times 10^5 \text{ cps}$) as the rinse time was increased to 90 s. A compromise of 60 s rinse time was therefore chosen in an effort to achieve a reasonable time per run as well as efficient removal of salt residue from the column.

By increasing sample loading time, and therefore signal intensity, the method detection limit can be improved as long as the column capacity is not exceeded and results are not blank

Table 3 Ag recovery experiments

Sample ID	Recovery (% , $n = 3$)	HCl concentration/M	Cl^- concentration (M) in final sample
0.1 ng ml^{-1} in DIW	101 ± 2	0.75	0.25
0.1 ng ml^{-1} in DIW	100 ± 1	0.50	0.16
0.1 ng ml^{-1} in 1% NaCl	99 ± 1	0.50	0.28
0.1 ng ml^{-1} SLEW-3	100 ± 1	0.50	0.34
0.1 ng ml^{-1} CASS-4	99 ± 1	0.10	0.39
0.1 ng ml^{-1} CASS-4	96 ± 1	0.50	0.52
0.1 ng ml^{-1} in 5% NaCl	97 ± 1	0.00	0.56
0.1 ng ml^{-1} 10% NaCl	65 ± 1	0.00	1.15

limited. The capacity of the mini-column for Ag was calculated to be 7500 μg , based on the stated Dowex 1-X8 resin capacity of 1.4 mequiv ml^{-1} . Although the Ag concentration in sea-water is very low, the total concentration of all anions in the sea-water matrix may exceed the column capacity and may affect Ag recovery as loading time increases. As shown in Fig. 5, response to Ag from the CASS-4 spiked at a concentration of 0.1 ng ml^{-1} increased linearly ($R^2 = 0.998$) with sample loading time up to 5 min (total volume of 20 ml). When the loading time exceeded 5 min, Ag response was no longer linear, a clear indication of severe competition for binding sites on the column. Although it is not necessary to restrict the loading time within the linear response range when isotope dilution calibration is used, a loading time of 3 min was chosen for subsequent study in an effort to achieve a reasonable time per run as well as to provide the possibility of using external calibration.

The effect of loading speed (or flow rate) on Ag response from CASS-4 sea-water was investigated. Subsamples of 10 ml of CASS-4 sea-water spiked at a concentration of 0.1 ng ml^{-1} were run on-line at different loading speeds in the range of 10–120 rpm (flow rates of 0.5–6 ml min^{-1}). To avoid passing excess HCl onto the column, this line was pinched at the moment the sample line ran dry. Good retention of Ag at all tested sample uptake rates was observed. A loading speed of 4 ml min^{-1} (80 rpm) was selected for subsequent study to achieve a reasonable time per run as well as to prolong the life time of the pump tubing by not running at maximum speed (6 ml min^{-1}).

As is evident from Table 2, each run can be completed in 6 min using the optimized experimental conditions, permitting a sample throughput of 10 h^{-1} , processing 12 ml volumes of sea-water. No decrease in efficiency of recovering of Ag on the Dowex 1-X8 mini column was observed after 800 runs.

Sea-water analysis

SLEW-3, CASS-2 and CASS-4 all have a 1000-fold higher concentration of Mo compared to Ag in these samples. A polyatomic $^{92}\text{Mo}^{16}\text{OH}^+$ interference on $^{109}\text{Ag}^+$ may thus hamper accurate Ag determination in sea-water using ICP-MS. The $^{107}\text{Ag}/^{109}\text{Ag}$ ratios in unspiked sea-water samples were therefore determined under optimum conditions established for on-line ICP-MS to investigate this effect. Ratios of 1.070 ± 0.007 (mean and one standard deviation, $n = 3$), 1.073 ± 0.007 ($n = 3$) and 1.071 ± 0.007 ($n = 3$) were obtained in SLEW-3, CASS-2 and CASS-4, respectively, in good agreement with the theoretical value of 1.076. This indicates

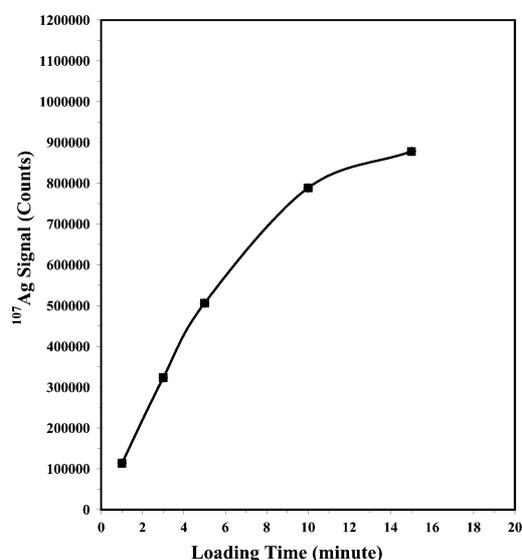


Fig. 5 Effect of sample loading time on Ag response.

that no significant interference on either Ag isotope arises with this methodology. Two standard solutions were also measured using this on-line ICP-MS method to further investigate potential interferences from $^{91}\text{Zr}^{16}\text{O}^+$, $^{90}\text{Zr}^{16}\text{OH}^+$, $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$ and $^{92}\text{Mo}^{16}\text{OH}^+$ on both Ag isotopes. A $^{107}\text{Ag}/^{109}\text{Ag}$ ratio of 1.076 ± 0.004 ($n = 4$) in the 0.1 ng ml^{-1} Ag standard solution containing 100 ng ml^{-1} of Zr and Mo and 10 ng ml^{-1} of Nb was obtained, in good agreement with a ratio of 1.076 ± 0.005 ($n = 3$) obtained with the 0.1 ng ml^{-1} Ag standard solution. This finding further confirms the efficient separation of Ag from interfering species.

Isotope dilution. The final analysis of sea-water samples was performed using an isotope dilution technique on subsamples taken from at least three different bottles of each sample. The following equation was used to quantitate the final Ag concentration:

$$C_x = C_y \cdot \frac{m_y}{m_x} \cdot \frac{A_y - B_y \cdot R_n}{B_x \cdot R_n - A_x} \cdot \frac{AW_x}{AW_y} \quad (1)$$

where C_x is the analyte concentration (ng ml^{-1}); C_y is the concentration of spike (ng ml^{-1}); m_y is the volume of spike used to prepare the blend solution of sample and spike (ml); m_x is the volume of sample used (ml); A_y is the abundance of the reference isotope in the spike; B_y is the abundance of the spike isotope in the spike; A_x is the abundance of the reference isotope in the sample; B_x is the abundance of the spike isotope in the sample; R_n is the measured reference/spike isotope ratio (mass bias corrected) in the spiked sample; AW_x is the atomic weight of analyte in the sample and AW_y is the atomic weight of the spike. Dissolved Ag concentrations of 1.93 ± 0.09 (mean and one standard deviation, $n = 10$), 5.15 ± 0.10 ($n = 3$) and 5.42 ± 0.08 ($n = 3$) pg ml^{-1} were obtained in SLEW-3, CASS-2 and CASS-4, respectively. The concentration of Ag determined in CASS-2 sea-water using the present on-line method agrees with the result of 5.2 ± 0.2 pg ml^{-1} reported by Smith and Flegal⁴ in 1993. They used a chelation-solvent extraction approach, based on ammonium 1-pyrrolidine dithiocarbamate and diethylammonium diethyldithiocarbamate (APDC-DDDC), with detection by GFAAS. It is evident that Ag remains stable in the CASS-2 sea-water for 8 years, when stored under cold (2 °C) and dark conditions. Samples of SLEW-3 were also monitored for stability, no difference being detected between the Ag concentration of 1.96 ± 0.12 pg ml^{-1} (mean and one standard deviation, $n = 3$) obtained recently using freshly opened bottles (stored in a cold and dark room) and a concentration of 1.92 ± 0.10 pg ml^{-1} ($n = 7$) determined two years earlier.

External calibration. Quantitative recovery of Ag spikes from sea-water samples on the Dowex 1-X8 column under optimum HCl concentration is evident from the data in Table 3. Dissolved Ag in SLEW-3 and CASS-4 was subsequently determined using an external calibration technique. For simplicity, 0.5 M HCl was merged with both sea-water samples and the calibration standards. Since a lower Ag recovery ($96 \pm 1\%$) occurs in CASS-4 at 0.5 M HCl, the final results were corrected to reflect this. Concentrations of 1.96 ± 0.10 pg ml^{-1} (mean and one standard deviation, $n = 3$) and 5.55 ± 0.15 ($n = 3$) pg ml^{-1} were obtained for dissolved Ag in SLEW-3 and CASS-4, respectively, in agreement with results generated by ID-ICP-MS. The ability to generate accurate data using a simple standard calibration curve attests to the overall ruggedness of this methodology.

Method blank. A concentration of 0.065–0.020 ($n = 3$) pg ml^{-1} was obtained for the sample blank using this on-line ID ICP-MS technique. This method blank was equivalent to 3% and 1% of the Ag concentration in SLEW-3 and CASS-4

sea-water, respectively. The final results should only be corrected for blanks contributed by the 0.5 M HCl, DIW rinse and the column itself. An experiment was designed to investigate the source of the method blank using DIW as sample measured on-line with the FIAS400 ICP-MS system. No difference was obtained for Ag response irrespective of whether DIW was admitted to the sample line or not (by pinching the sample line). This confirmed that the blank arose principally from the 0.5 M HCl and column itself; not from the DIW "carrier" that was conveniently used to prepare the sample blanks. Therefore, the final Ag concentrations in all sea-water samples were corrected for a blank of 0.065 pg ml^{-1} .

Detection limits. Two detection limits were derived for this on-line flow injection ICP-MS method under optimum experimental conditions. A value (3σ) of 0.056 pg ml^{-1} was estimated from the standard deviation of the mean of Ag concentrations derived from ten replicate measurements of a sample blank (pH 1.6 DIW) based on the measured intensity of the ^{107}Ag isotope by external calibration. For the ID-ICP-MS technique, three ^{109}Ag spiked sample blanks were used to estimate a method detection limit of 0.059 pg ml^{-1} based on three times the standard deviation of calculated concentrations. It is evident that both procedures yield comparable detection limits, which are superior to previously published methods.^{3,4,6,9-11}

Sediment analysis

Isotope dilution. As expected, a much higher $^{107}\text{Ag}/^{109}\text{Ag}$ ratio of 1.767 ± 0.006 ($n = 3$) was obtained when measuring samples of unspiked MESS-3 digest without column separation, compared to the expected value of 1.076. MESS-3 has a much higher Zr, Mo and Nb content compared to sea-water, giving rise to severe polyatomic interferences from $^{91}\text{Zr}^{16}\text{O}^+$ and $^{90}\text{Zr}^{16}\text{OH}^+$ on $^{107}\text{Ag}^+$ and less severe interferences from $^{93}\text{Nb}^{16}\text{O}^+$, $^{92}\text{Zr}^{16}\text{OH}^+$ and $^{92}\text{Mo}^{16}\text{OH}^+$ on $^{109}\text{Ag}^+$, as indicated by the elevated $^{107}\text{Ag}/^{109}\text{Ag}$ ratio. These interferences must be eliminated in order to obtain accurate results. A $^{107}\text{Ag}/^{109}\text{Ag}$ ratio of 1.074 ± 0.005 ($n = 3$) was obtained in unspiked MESS-3 digest processed off-line on the Dowex 1-X8 column, as described under the Procedure for sediment analysis. This finding confirmed that a good separation of Ag from the sediment matrix had been achieved. The final analysis of MESS-3 sediment was performed on six replicate digests. A concentration of 0.169 ± 0.002 ($n = 6$) $\mu\text{g g}^{-1}$ was obtained in MESS-3, in agreement with the certified value of $0.18 \pm 0.02 \mu\text{g g}^{-1}$.

External calibration. Lower than expected response from Ag in the eluent obtained from off-line column separation of a 10 ml volume of 10-fold diluted MESS-3 digest was observed during ID-ICP-MS measurement. A spike recovery experiment using a spiked concentration of 1 ng ml^{-1} for 10 ml of a 10-fold diluted MESS-3 digest confirmed a low recovery of $32 \pm 2\%$ ($n = 3$). This may be attributed to saturation of the Dowex 1-X8 column. Although low recovery does not affect Ag determination using the ID-ICP-MS or standard additions techniques, quantitative recovery is required for accurate results using external calibration. Two further spike recovery experiments were conducted using much less digest in an effort to avoid column saturation. A 10 ml volume of 100-fold diluted and a

10 ml volume of 200-fold diluted MESS-3 digest at spiked concentrations of 1 and 0.5 ng ml^{-1} , respectively, were used for these spike recovery tests. Recoveries of $91 \pm 1\%$ ($n = 3$) and $98 \pm 2\%$ ($n = 3$) were obtained for the 100-fold and 200-fold diluted MESS-3 digests, respectively. Thus, 100-fold and 200-fold diluted MESS-3 digests were used for Ag determination *via* the on-line method (described under the Procedure for sea-water analysis) with external calibration for quantitation. The recoveries noted above were used to correct final Ag concentration, yielding values of 0.185 ± 0.010 ($n = 3$) and 0.181 ± 0.004 ($n = 3$) $\mu\text{g g}^{-1}$ in MESS-3, based on the 100-fold and 200-fold diluted digests, respectively. These results are also in good agreement with the certified value of $0.18 \pm 0.02 \mu\text{g g}^{-1}$.

Conclusion

A fast (6 minutes per run), accurate on-line flow injection method for the determination of silver in sea-water using isotope dilution inductively coupled plasma mass spectrometry has been developed. The method achieves a sufficiently low detection limit (0.06 pg ml^{-1}) that it is well suited for quantitation at the few pg ml^{-1} level of Ag concentration typically found in sea-water. Accurate results can, in addition, be achieved by external calibration using this on-line method, which can also be applied to the analyses of sufficiently diluted digests of marine sediments, as the column serves to eliminate all potentially interfering spectroscopic interferences. The methodology should be very useful for monitoring Ag levels in natural water and sediment for the study of Ag toxicity effects on bio-organisms in oceanographic research and survey work.

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