Flow-Injection Inductively Coupled Plasma Mass Spectrometer Incorporated with an Ultrasonic Nebulizer-Membrane Dryer: Application to Trace Lead Detection in Aqueous Solution and Seawater

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Flow-injection (FI) incorporated with inductively coupled plasma mass spectrometry (ICP-MS) was used to determine lead in aqueous solutions and seawater. Lead was retained in the form of Pb-DDPA complex in a sorbent microcolumn packed with C_{18}-bonded silica, and then carried to an ultrasonic nebulizer with methanol as eluent. The ultrasonic nebulizer removed about 66% of methanol solvent vapors from entering the detector. A multi-tube Nafion® membrane dryer, installed along the passage prior to the ICP torch, further removed 50% of methanol. Reducing the amount of methanol solvent significantly improved the signal-to-background ratio of the detector. Accordingly, when the sample was loaded for 15 and 60 s, respectively, Pb detection limits were determined to be 0.162 and 0.028 ng/L, one to two orders of magnitude lower than those reported. The enrichment factors were also measured to be 7 and 28, with the sampling frequencies of 31 and 21 h^{-1}, respectively. The method was applied for the determination of Pb in a reference seawater. The obtained result was 0.013 ± 0.001 ng/mL, consistent with the certified value of 0.013 ± 0.005 ng/mL.

Index Headings: **Inductively coupled plasma mass spectrometer; Ultrasonic nebulizer; Membrane dryer; Lead detection.**

INTRODUCTION

Lead is a cumulative poison, and even trace levels may cause long-term health risks. Unfortunately, lead contents entering the environment have recently been increasing. Some sources including antiknock reagent used in gasoline, smelting operation, and combustion of coal have contributed greatly to lead pollution.[1,2] Developing sensitive methods to determine trace amounts of lead contained in the biological and environmental samples has gained importance.

Thus far, a number of spectroscopic techniques such as flame atomic absorption spectrometry (FAAS),[3–6] graphite furnace atomic absorption spectroscopy (GFAAS),[7,8] spectrophotometry,[9–11] electrothermal (ET) atomization,[12,13] conductimetry,[14,15] inductively coupled plasmas optical emission spectroscopy (ICP-OES),[16,17] and inductively coupled plasma mass spectroscopy (ICP-MS)[18–20] have been widely applied to the determination of Pb. Flow-injection (FI) analysis has been popularly combined with the above techniques. FI methods are advantageous for merits of high sample throughput, limited sample handling, rapid sampling frequency, high reproducibility, low sample consumption, and low contamination risk.[21,22] In addition, an FI system may incorporate an in-line chromatographic-like kit to separate the analyte from interfering matrices and to concentrate its content for accurate determination.[22] An FI manifold coupled with AAS has been used to determine lead in aqueous solutions or seawater with detection limits in the range of 0.5–10 ng/mL.[3,23,24] When ETAAS is used instead, it has been found that the limit of Pb detection may be lower by approximately two orders of magnitude.[12,25]

The ICP-MS is a sensitive technique recently adopted in elemental trace analysis. The technique has the advantages of simultaneous (or sequential) multielemental analysis and extremely sensitive detection for the charged analyte species.[26,27] While taking advantage of the merits of FI preconcentration and separation, FI-ICP-MS in lead determination should be more sensitive than or comparable to those techniques described above. However, when an FI sorbent extraction system is coupled, the problem of dealing with excess organic solvent will be encountered. The sorbent extraction column is usually packed with C_{18}-bonded silica, in which various lead complexes can be sorbed. Ethanol or methanol usually serves as the eluent to remove the complexes to the detector. The chelating reagents often used in the C_{18} column are summarized in Table I.

When excess organic solvents enter the ICP-MS, severe interference may occur. First, polyatomic ions may cause isobaric interference and reduce the detection sensitivity. Second, the induced space charge effect will disperse the amount of analyte ions into the detector. Third, particulate carbon may easily contaminate the torch tube, sampler cone, skimmer, and ion lenses to degrade the experimental reliability. Further, excess organic solvent may destabilize or even extinguish the ICP torch. For this reason, several methods including back extraction,[28,29] cryogenic desolvation,[30–32] and membrane desolvation[33–36] have been developed to overcome these problems. Among them, the back extraction method introduces an appropriate reagent to extract the sample back to the water phase. This process is time-consuming and easily causes sample loss and contamination. The cryogenic desolvation method makes use of the heating-and-cooling cycle to remove the solvents with low boiling points. The membrane desolvation method applies a membrane to separate the aerosol stream from the solvent vapors, which are purged through the membrane tube and removed by using an argon counter gas.

In this work, we have applied FI-ICP-MS to determine trace lead from aqueous solutions. The FI manifold con-

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TABLE I. Chelating reagents frequently used in the C_{18} microcolumn for trace metal determination.

Reagent[a]	Analytes	Eluent	Sample	Detection method	Ref.
8-HQ	Cu, Mn	MeOH	Seawater	ICP-AES	41
8-HQ	Co, Cd, Zn, Ni, Mn, Fe	MeOH	Seawater	FAAS	42
8-HQ	Cu, Pb	MeOH	Water	FI-AAS	43
PAR	Cu	EtOH	Water	FI-AAS	43
Ferrozine	Fe (II)	MeOH	Seawater	FI-spectrophotometry	44
DDTC	Cr	EtOH	Natural water	FI-GFAAS	45
HDEHP, H_2MEHP	rare earth	HC1	Seawater	ICP/M	46
DDDC, DDPA	Cd, Cu, Pb	MeOH	Digested soil	FI-AAS	47
Ferrozine	Fe (II)	MeOH	Water	FI-AAS	48
ADPC	Pb	MeOH	Seawater	FI-GFAAS	49
5-Br-PAPS	Cd, Mn, Pb, Cu, Ni, Zn, Fe	HNO_3	Seawater	FI-ICP/MS	20
DDTP	Cu, Cd, Pb, Bi, Se	MeOH	Seawater	FI-ETV-ICP/MS	19
DDTP	Cu, As, T1, Se, Cd, In, Hg, Pb, Bi	MeOH	Water, urine, river water, bovine liver, bovine muscle	FI-ICP/MS	18

[a] DDPA = DDTP (sodium or ammonium salts of *O,O*-diethyldithiophosphoric acid); DDDC (diethylammonium-*N,N*-diethyldithiocarbamate); HEDEHP [bis(2-ethylhexyl)hydrogen phosphate]; DDC (diethyldithiocarbamate); PAR [4–(2-pyridylazo)resorcinol]; H_2MEHP (2-ethylhexyl dihydrogen phosphate); 8-HQ (8-hydroxyquinoline); APDC (ammonium pyrolidinedithiocarbamate); PAN [1–(2-pyridylazo)–2-naphthol]; 5-Br-PAPS [2–(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamion)phenol].

tained a C_{18}-column to retain the Pb-DDPA (ammonia diethyl dithiophosphate) complex. Methanol was used as eluent. To eliminate excess methanol vapor into the detector, we used an ultrasonic nebulizer-Nafion® multi-tube membrane desolvator. The Nafion® membrane, different from those with microporous structure, takes advantage of a bonded functional group to selectively absorb polar solvents, which are then removed by the sweep gas.[37] About 83% of the methanol eluent can be removed by the desolvation system. Accordingly, a detection limit of 0.028 ng/L was achieved for Pb. The method was successfully applied to determine Pb in a reference seawater.

EXPERIMENTAL

ICP-MS Apparatus. A SCIEX ELAN 6000 ICP-MS (Perkin-Elmer, USA) was used for all data acquisition. It was run in sequential mode, peak hopping to masses of interest. An ultrasonic nebulizer (U-5000 AT, Cetac, USA) served as a sprayer for sample introduction. The sample was pumped onto the surface of a piezoelectric crystal, which vibrated to generate dense but homogeneous aerosols. By making use of the heating-and-cooling cycle, the ultrasonic nebulizer could partially remove the organic solvent from entering the detector. In an effort to avoid conductive coupling between the load coil and the plasma, both ends of the load coil were biased with high voltage of equal amplitude but opposite phase. The plasma potential induced by the net radio-frequency (rf) power may then be minimized to a few volts. The sampling depth between the sampler tip and the top coil was fixed at 9 mm for all data acquisition. The coolant gas flow rate, the auxiliary gas flow rate, and the aerosol gas flow rate were fixed at 15.0, 1.0, and 0.8 L/min, respectively, throughout the experiment. The rf power was optimized at 1200 W.

Reagent. Deionized water (Millipore, USA) was used for the preparation of solutions. Methanol (HPLC grade) was obtained from Mallinckrodt, DDPA (reagent grade) was from Aldrich, HNO_3 (Trace Pur grade) was from Merck, and NaOH (reagent grade) was from Chameleon, Japan. A standard solution of 1000 ppm lead (Merck, Germany) was purchased and diluted to various concentrations used. Certified seawater (NASS-4, National Measurement Standard) was from the National Research Council, Canada.

FIA Operation. As displayed in Fig. 1, the FI manifold consisted of two four-channel peristaltic pumps (MC-MS CA4, Ismatec, Switzerland), three four-port low-pressure Teflon® solenoid valves, and two microcolumns (Sep-Pak C_{18} cartridge, Millipore), each packed with C_{18}-bonded silica gel. The first microcolumn was used to remove metal contaminant present in the DDPA chelating reagent, while the second one was used to preconcentrate lead and minimize the matrix interference. Silica tube was used to carry the methanol solvent, while Tygon® tubes were used for the remaining carrier streams. The pump tubes were replaced frequently to ensure that the flow rates were kept constant. The PTFE reaction coil (0.76 mm i.d. and 50 cm long) was knotted to minimize the dispersion of carrier streams and facilitate the chelating reaction.

A mode of time-limited control was used for the sam-

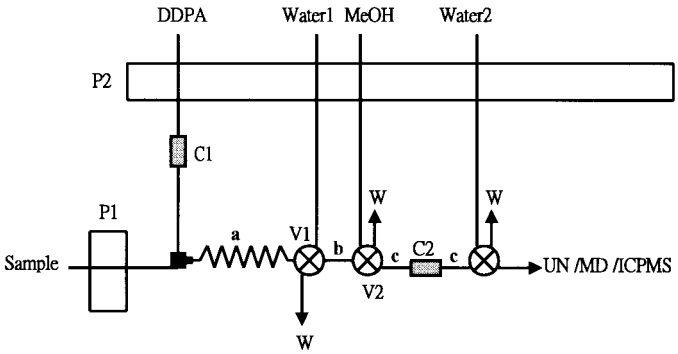

FIG. 1. Schematic diagram of the flow-injection manifold. **P1** and **P2** denote peristaltic pumps; **C1**, C_{18} microcolumn for DDPA purification; **C2**, C_{18} microcolumn for preconcentration/separation; **V1–V3**, solenoid valves; **W**, waste. Coil length for **a**: 50 cm, **b**: 3 cm, and **c**: 2 cm.

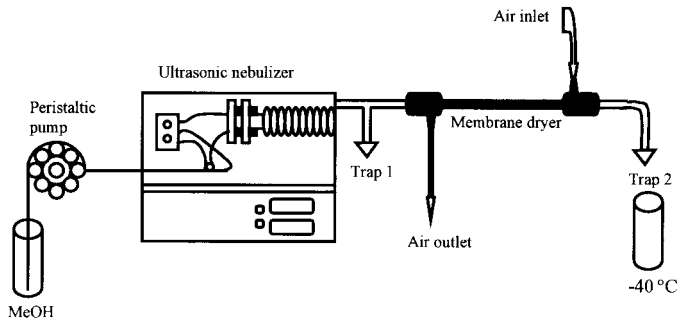

FIG. 2. Design for evaluation of the desolvation efficiency for ultrasonic nebulizer and Nafion® membrane dryer. In step 1, when the open end is blocked, the methanol collected in trap 1 can be used to evaluate the desolvation efficiency of the ultrasonic nebulizer. In step 2, trap 1 is blocked and the open end is then connected to the Nafion® membrane dryer. The methanol collected in trap 2, subtracted from that collected previously in trap 1, can be used to evaluate the desolvation efficiency of the Nafion® membrane dryer.

ple loading in the FI manifold. Before the sample was loaded, two microcolumns were activated with the methanol and then rinsed for 15 min with the deionized water. Various concentrations (0.05–5 ng/mL) of Pb aqueous solutions were loaded at a flow rate of 3 mL/min for 15 or 60 s, corresponding to a volume of 0.75 or 3 mL. DDPA solution was flowed at 1 mL/min for 10 s. The Pb and DDPA solutions were well mixed along a knotted reaction coil, and the resultant Pb-DDPA complex was retained in the C_{18} column. The complex was rinsed with the deionized water at a flow rate of 1 mL/min for 15 s to remove the excess reagents. Then the complex was eluted with the methanol at a flow rate of 1 mL/min for 9 s to the ultrasonic nebulizer. Before the next sample loading, the microcolumn was washed with the methanol at 1 mL/min for 20 s and then the deionized water at 1 mL/min for 20 s.

A Nafion® multi-tube membrane dryer (Perma Pure Co.) was installed prior to the ICP torch to further remove the organic solvent. This Nafion® membrane is composed of Teflon® structure with a side chain bonded to a functional group of perfluoro-3,6,-dioxa-4-methyl-7-octene-sulfonic acid.[37] It is capable of resisting against high temperature up to 160 °C. The bonded sulfonic acid can feasibly absorb water and some selective organic solvents without causing significant analyte loss. The membrane dryer contains multiple Nafion® micro-tubes packed together as the inner cylinder, which the aerosol stream and organic solvent vapors are driven through. A large fraction of the solvent vapors is absorbed on the surface and removed by a counter gas flowing through the outer cylinder. Note that the Nafion® membrane allows air to be used as sweep gas. In contrast, for those made of microporous materials, Ar gas should be used to keep the ICP torch stable.[33–36]

RESULTS AND DISCUSSION

Desolvation Efficiency. As shown in Fig. 2, the desolvation efficiency for the ultrasonic nebulizer-Nafion® membrane dryer can be evaluated with the bench method. First, methanol was pumped at 1.2 mL/min to the ultrasonic nebulizer and collected at trap 1 (with the other open end blocked; see Fig. 2) into a Dewar trap containing pieces of polyethylene (PE) chips at temperature of −40 °C. The use of PE chips increased the surface area and thus the collection efficiency for the methanol. The methanol collection was done three times every 10 min. As heating and cooling conditions of the nebulizer were optimized at 140 and 4 °C, respectively, the relationship for methanol removal in time is given in Fig. 3. The desolvation efficiency of the ultrasonic nebulizer can thus be determined to be 66%, considering the nebulization efficiency as 30%.

After the ultrasonic nebulizer was characterized, the membrane dryer was connected to the open end (with trap 1 blocked; see Fig. 2). The dryer is surrounded with a heating tape at a temperature adjustable from 40 to 130 °C. The air is driven at 2.0 L/min, counter to the methanol stream direction, through the outside wall of the membrane tube. As the methanol vapors pass through the dryer, a large fraction may be absorbed on the membrane surface and then desorbed by the sweep gas. The residual solvent was collected at trap 2 in a similar trap with PE chips at −40 °C. The desolvation efficiency of the membrane dryer could be evaluated from the weight difference of methanol collected at traps 1 and 2. The calibration curve for the removed methanol weight within 50 min is also shown in Fig. 3, indicating that the desolva-

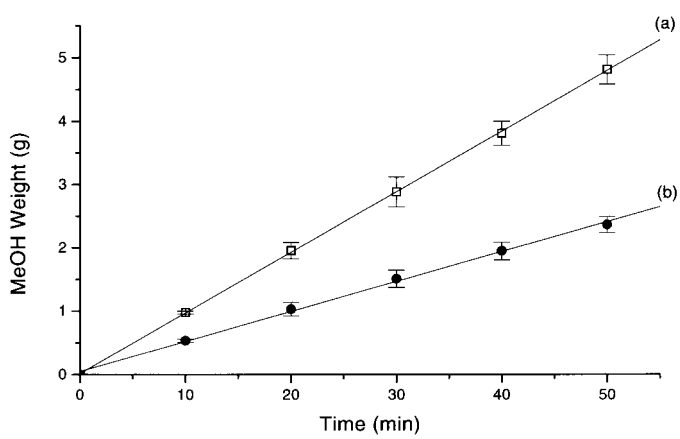

FIG. 3. Collected methanol weight within 50 min by using (***a***) ultrasonic nebulizer and (***b***) Nafion® membrane dryer, respectively. Conditions: sample flow rate, 1.2 mL/min; carrier gas flow rate, 1.0 L/min; membrane temperature, 100 °C, and membrane sweep gas flow rate, 2 L/min.

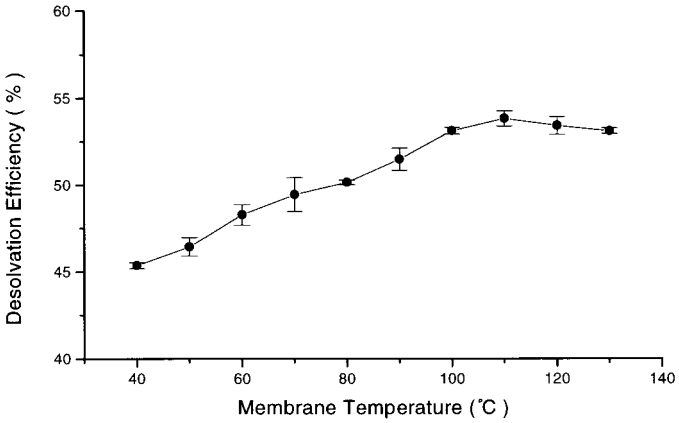

FIG. 4. Desolvation efficiency of Nafion® membrane dryer as a function of membrane temperature. Conditions: sample flow rate 1.2 mL/min; carrier gas flow rate, 1.0 L/min; and membrane sweep gas flow rate, 2 L/min.

tion system can remain very stable for a long time. The desolvation efficiency of the membrane dryer was determined as a function of the membrane temperature ranging from 40 to 130 °C, as shown in Fig. 4. The maximum desolvation efficiency was about 53% at 110 °C.

Optimization of FI-ICP-MS. The FI conditions were optimized in an attempt to obtain a complete chemical reaction in the coil, sufficient adsorption of the resultant chelating complex on the microcolumn, limited dispersion in the eluting process, and a large enrichment factor. After optimizing these conditions, we sought the determination of Pb in aqueous solutions to find the enrichment factor, sampling frequency, dynamic range of concentration, precision, and detection limit.

The sample and the blank count rates (cps) were measured, due to the fact that the ^{208}Pb S/B (signal-to-background) (blank) ratio obtained is sensitive to factors including the loading rate, concentration, and pH condition of DDPA, the sample loading rate, and the methanol elution rate. For optimizing these conditions, the ^{208}Pb S/B ratio was measured as a function of one parameter, while the remaining conditions were fixed. For instance, Fig. 5a shows the ^{208}Pb S/B ratio as a function of the methanol elution rate under the conditions of DDPA, prepared at pH 1, 0.2% (w/v) concentration, with a flow rate at 1 mL/min and the sample loading rate at 3 mL/min. The Pb intensity reached a plateau when the methanol flow rate was increased to 1 mL/min and thus this value was adopted throughout the work. Similar procedures were applied to find the optimal conditions for the other parameters. The optimized conditions are summarized in Table II. Note that the stability of the Pb-DDPA complex is affected by the pH condition of the DDPA solution. To simplify the introduction of the reagents into the detector, we adjusted the related pH values by the addition of HNO_3 or NaOH without the use of buffer solution. For instance, the DDPA solution at pH 2 could be prepared by dissolving an appropriate weight of DDPA in 0.01 M HNO_3 solution. Figure 5b shows that the measured Pb intensity decreases with increasing the pH value. The complex stability degrades by 8-fold as the solution is at pH 7. In addition, as shown in Fig. 5c, one finds that the methanol eluted for 9 s is enough to completely remove

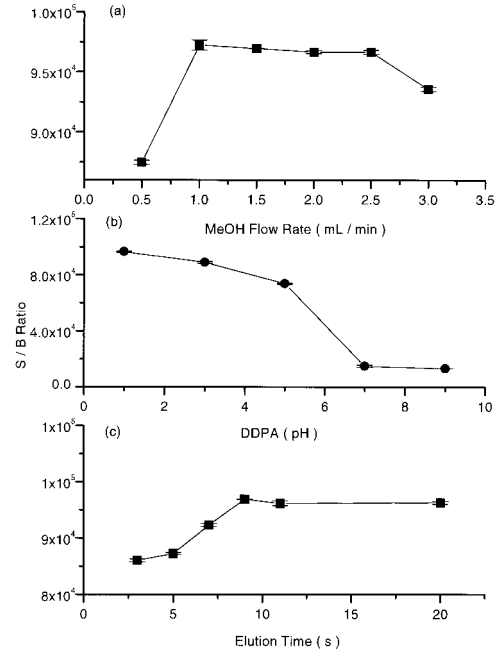

FIG. 5. FI conditions: (**a**) methanol flow rate; (**b**) pH condition of DDPA solution; and (**c**) methanol elution time, optimized for the lead determination by ICP-MS. The signal-to-background ratio is defined as a ratio of the sample count rate to the blank count rate.

the Pb-DDPA complex from the C_{18} column. For avoiding particulate carbon deposition on the detection system, we kept the solvent elution time at 9 s.

Methanol Effect on ICP-MS Detection. Excess methanol solvent in the ICP-MS detection can cause serious problems, whereas a small amount does enhance the sensitivity. To examine this effect, we prepared various fractions (v/v) of methanol contained in water. For minimizing the carbon contamination, a volume of only 250 μL

TABLE II. Parameters optimized for operation of FI-ICP-MS incorporated with a desolvator.

Parameter	Condition
FI	
Sample loading rate	3 mL/min
DDPA loading rate	1 mL/min
MeOH elution rate	1 mL/min
Water rinsing rate	1 mL/min
DDPA concentration	0.2% (w/v)
DDPA pH	1
MeOH elution time	9 s (150 μL)
UN-MD[a]	
UN heater temperature	120 °C
UN condenser temperature	4 °C
MD membrane temperature	100 °C
MD sweep gas flow rate	2.0 L/min
ICP/MS	
RF forward power	1200 W
AC rod offset	−4.5 V
Coolant gas flow rate	15.0 L/min
Auxiliary gas flow rate	1.0 L/min
Aerosol gas flow rate	0.8 L/min
Measurement mode	Peak hopping
Signal measurement	Peak area
Sweep/reading	20
Replicates	10

[a] UN-MD denotes ultrasonic nebulizer-membrane dryer.

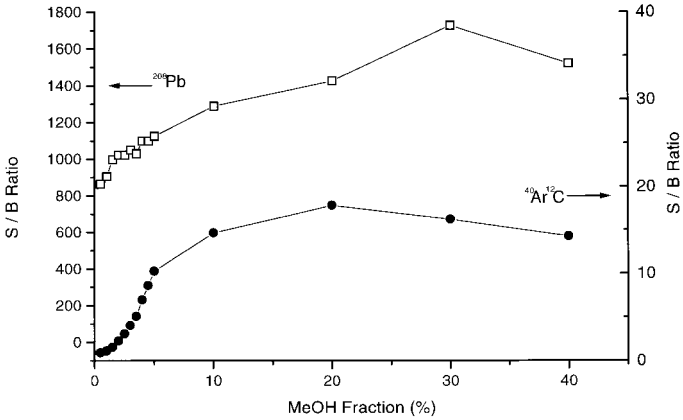

FIG. 6. Signal-to-background ratio of ^{208}Pb and ^{40}Ar^{12}C detection as a function of methanol fraction, which indicates a volume ratio of methanol to water.

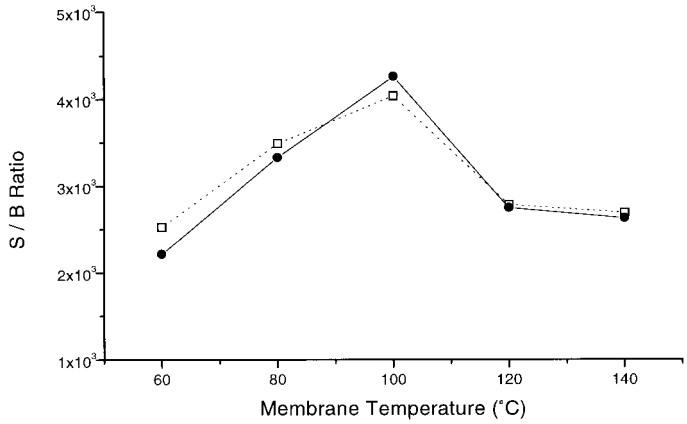

FIG. 7. Signal-to-background ratio of ^{208}Pb detection as a function of membrane temperature. The solid line indicates the S/B ratios obtained following the experimental procedure of increasing temperature. The dashed line indicates the S/B ratios obtained following the experimental procedure of decreasing temperature.

for each methanol fraction was pumped into a pneumatic nebulizer, with which the methanol/water ratio remained almost invariant prior to the detection. As the methanol fraction was increased to 30%, Fig. 6 shows that the ^{208}Pb intensity was enhanced to the maximum, about twice that achieved under the conditions without methanol. When the fraction was less than 40%, the plasma condition remained very stable. A reliable ^{208}Pb S/B ratio could be obtained from the measurement either along the direction of increasing methanol fraction or along the reversed direction. However, the torch would be extinguished as the fraction exceeded 60%. To find whether the $^{40}Ar^{12}C^+$ matrix was related to the methanol added, the $^{40}Ar^{12}C^+$ intensity was similarly measured (Fig. 6). The $^{40}Ar^{12}C^+$ intensity, approaching the maximum at the methanol fraction of 20%, was roughly proportional to the methanol concentration within only a small fraction range (5%). The reaction complexity of $^{40}Ar^{12}C^+$ apparently increased at higher concentrations.

Optimization of ICP-MS Coupled with Membrane Dryer. In the preceding section, the membrane dryer was characterized for its desolvation efficiency. Nevertheless, the conditions for the maximum desolvation efficiency may not lead to the best sensitivity for the accurate determination of Pb by ICP-MS. As shown in Fig. 7, the optimal membrane temperature for the best ^{208}Pb S/B ratio detection was at 100 °C, slightly different from 110 °C for the maximum desolvation efficiency. The membrane dryer at 100 °C may further remove 50% of the methanol vapors out of the aerosol stream as introduced from the ultrasonic nebulizer. Therefore, the total desolvation efficiency amounts to 83% with the use of the ultrasonic nebulizer-Nafion® membrane dryer system. The optimal conditions for FI-ICP-MS with the desolvation system are summarized in Table II, as characterized with loading of a 100 μL of 30 ng/mL Pb aqueous solution. Since the Nafion® membrane is not made of microporous material, the air used as the sweep gas cannot diffuse through the wall to cause the ICP turbulence. Nevertheless, its flow rate has significant impact on the detection sensitivity. For instance, the optimal flow rate at 2 L/min enhances the ^{208}Pb S/B ratio twice as much as compared with that at 0.5 L/min.

We also compared Pb detection sensitivity between cold plasma and normal plasma temperature. As shown in Fig. 8, the rf power at 1200 W leads to a ^{208}Pb S/B ratio that is better by threefold than that at 700 W. One should note that reducing the plasma temperature may decrease both the sample ion concentration and the polyatomic ion matrices such as ArO^+ and ArH^+. For heavy atoms such as ^{208}Pb, the isobaric interference becomes less important. Reduction of the polyatomic ion concentration may not significantly contribute to the S/B ratio enhancement. On the contrary, if light atoms such as ^{40}K and ^{56}Fe are monitored, the cold plasma condition might increase the detection sensitivity.[38,39] Note that the cold plasma condition should be accompanied by a concurrent increase in the aerosol gas flow rate. In this work the aerosol gas flow rate was fixed at 0.8 L/min, the same as in the normal plasma condition. Thus the plasma temperature may not be as cold as expected.

Determination of Pb in Aqueous Solution. The optimized conditions are listed in Table II. Various concentrations in the range from 0.05 to 5 ng/mL were loaded for 15 and 60 s, respectively. The calibration curve mea-

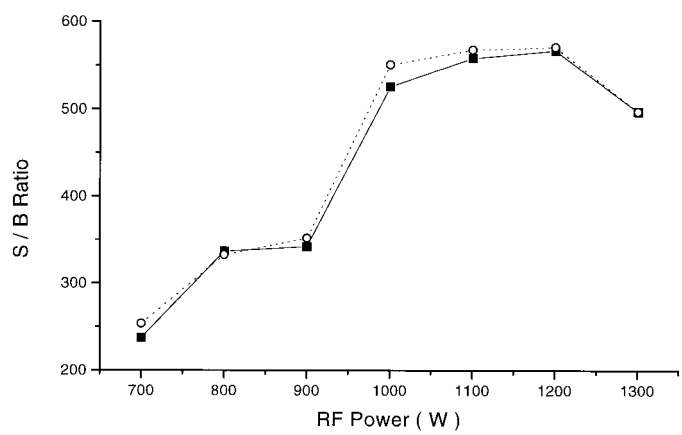

FIG. 8. Radio-frequency power dependence of ^{208}Pb signal-to-background ratio obtained by FI-ICP-MS with desolvation system installed. The solid line indicates the S/B ratios obtained following the experimental procedure of increasing rf power. The dashed line indicates the S/B ratios obtained following the experimental procedure of decreasing rf power.

TABLE III. Comparison of spectroscopic methods for Pb determination.

Spectroscopic method	FI-CP/MS[a]	FI-ETV-ICP/MS[b]	FI-TLEI[c]	FI-ICP/MS[d]	
Desolvation system	None	None	None	Ultrasonic-membrane	
Sample	Biological, environmental	Seawater	Seawater	Seawater	
Nebulizer	Pneumatic	ETV	Pneumatic	Ultrasonic	
Chelating agent	DDPA	DDPA	DDPA	DDPA	
Eluent	MeOH	MeOH	MeOH	MeOH	
Eluent consumption (μL)	100	25	>9000	150	
Sample loading (s)	60	60	300	15	(60)
Sample consumption (mL)	2.3	2.3	15	0.75	(3)
DDTP consumption (mL)	1.65	1.1	7.5	0.417	(1.16)
DDTP concentration % (w/v)	0.6	0.6	0.2	0.2	
Sampling frequency (h^{-1})	21	22	9	31	(21)
Linear range (ng/mL)	0.05–0.5	0.0125–0.1	0.025–1000	0.05–5	
Enrichment factor	22	132	48	7	(28)
Detection limit (ng/mL)	4.5	0.3	3.3	0.16	(0.028)
Correlation coefficient	0.9998	0.9990	Not informed	0.9996	(0.9973)
Precision (%)	4.3	<10	Not informed	5.7	(5.3)
Pb in seawater (NASS-4)	Not informed	0.014 ± 0.005	0.0112 ± 0.0006	0.013 ± 0.001	(0.013 ± 0.001)

[a] Reference 18.
[b] Reference 19.
[c] Reference 40.
[d] This work.
[e] The certified value of NASS-4 is 0.013 ± 0.005 ppb.
[f] Data in the parentheses are obtained at 60 s loading time.

surements indicate that the linear dynamic range extends from 0.05 to 5 ng/mL, yielding a slope of 226 and 963 for the 15 and 60 s loading times, respectively. The detection limits for Pb, as the ratio of three times standard deviation (3σ) of the blank measurement to the slope of the calibration curve, were 0.162 and 0.028 ng/L for the conditions of 15 and 60 s sample loadings, respectively. The enrichment factor is theoretically defined as the ratio of the analyte concentration in the concentrate to that in the original sample. But its value may be practically estimated to be the ratio between the slopes of the calibration curves obtained with and without the preconcentration procedure.[22] The enrichment factors thus obtained were 7 and 28 with sampling frequencies of 31 and 21 h^{-1}, respectively. Note that the above data were obtained with the methanol elution time adjusted to only 9 s, corresponding to 150 μL.

As compared with other techniques used for the Pb determination, our detection limits are lower by at least one order of magnitude. A comparison among several spectroscopic methods is listed in Table III. Among them, the approach used by Dressler et al. employed an FI-ICP-MS apparatus, similar to ours but without a desolvator.[18] In their measurement, the use of a pneumatic nebulizer with only 1–3% nebulization efficiency degraded the signal sensitivity. In addition, without incorporation of a methanol desolvator, the mass spectrometer suffered seriously from the organic solvent interference. Thus, their detection limit was higher by two orders of magnitude. The authors of the same group used an FI-ETV-ICP-MS apparatus and obtained a better detection limit of 0.3 ng/L, which was an order of magnitude higher than ours.[19] Although ETV is a very effective method for the sample introduction, solvent interference may degrade the signal-to-noise ratio. The adoption of 0.6% (w/v) DDPA, three times higher concentration than in this work, to form complexes with multiple elements may also contribute to the background noise. In a comparison of the measurements between flow-injection two-step laser-enhanced ionization (FI-TLEI) and this work, the FI-TLEI was insensitive to the matrix interference and exhibited a larger linear dynamic range of concentration.[40] But the detection limit was worse by two orders of magnitude, in spite of the consumption of five times more sample volume.

Determination of Pb in Seawater. The concentration of Pb in seawater was determined by using the standard addition method. With the conditions optimized with standard solutions, seawater (NASS-4) was loaded for 15 and 60 s, respectively, corresponding to 0.75 and 3 mL, and then analyzed with ICP-MS coupled with an ultrasonic nebulizer-membrane dryer for Pb. Five additions of standard analyte ranging from 50 to 500 ng/L were made to yield a straight line. Since a linear calibration was obtained, the addition of Pb standard solutions should not significantly affect the Pb-DDPA complex retained in the microcolumn. The residual DDPA reagent and other matrices such as alkali and alkaline earth salts were rinsed out of the Pb-DDPA complex with the deionized water at a flow rate 1 mL/min for 15 s wash time, as described previously in terms of FIA operation. The results were 0.013 ± 0.001 and 0.013 ± 0.001 ng/mL for the 15 and 60 s loading time, respectively. The results agreed with the certified value of 0.013±0.005 ng/mL.

CONCLUSION

We have employed FI-ICP-MS in combination with an ultrasonic nebulizer-Nafion® membrane dryer to determine Pb in aqueous solution and seawater. By taking advantage of preconcentration and separation merits of FI and desolvation capability of the desolvator, we achieved a lower Pb detection limit. Several results are summarized as follows:

1. A total amount of 83% of the methanol solvent was removed from entering the plasma by installing the desolvation system prior to the ICP torch. Reduction of the methanol solvent was advantageous in eliminating the plasma disturbance, reducing the polyatom-

ic ion matrices and background noise, and avoiding contamination of the detection system.
2. The sample and eluent consumed were confined to a small amount for minimizing the system contamination and interference but increasing the sampling frequency. That approach led to small enrichment factors of 7 and 28 as sample was loaded for 15 and 60 s, respectively. Nevertheless, the detection limits for Pb from aqueous solutions reached 0.162 and 0.028 ng/L—lower by 1–2 orders of magnitude than those reported with similar techniques.

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