Notes

Multiple-Element Detection in Aqueous Solution and Seawater by Using an On-line Preconcentration Method for Inductively Coupled Plasma Mass Spectrometry

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Inductively coupled plasma–mass spectrometry (ICP-MS) incorporated with an on-line preconcentration system was used to determine trace amounts of ten metals including Ni, Cu, Zn, Rh, Ag, Cd, In, Au, Tl, and Pb in aqueous solutions and seawater. These metals, which formed the complexes, were retained in a sorbent microcolumn, followed by elution with methanol through a desolvation unit, which was capable of removing 83% of methanol. The limits of detection for these elements were determined simultaneously to be in the range from 3 to 20 ng/L.

Introduction

Trace heavy metals contained in biological and environmental samples may cause long-term health problems.[1,2] A number of spectroscopic techniques have been widely applied for trace amount determination. Among them, inductively coupled plasma mass spectroscopy (ICP-MS) has the advantages of simultaneous multi-elemental analysis and extremely sensitive detection for charged analyte species.[3-5] While combining with an on-line preconcentration system,[6-8] the ICP-MS may further enhance its detection sensitivity. Although ion-exchange resins have usually been adopted for matrix separation and sample preconcentration in aqueous solution,[9-12] in this work we focused on the liquid–solid sorbent extraction method as an alternative, and employed a desolvation system to improve the operation efficiency.

In the sorbent extraction method, analyte complexes may be sorbed on low polarity solid materials, and then eluted with an organic solvent.[13-17] When excess organic solvents enter the ICP-MS, severe interference may occur. The membrane desolvantion method is one of the effective methods to take away a large amount of organic solvent. This method applies a membrane to separate the aerosol stream from the solvent vapors.[18-20] Nevertheless, the membrane with microporous structure lacks chemical selectivity so as to cause some analyte losses, and requires Ar as the sweep gas to keep the ICP torch stable. As an alternative desolvation system, an ultrasonic nebulizer-Nafion multi-tube membrane desolvator, incorporated with an on-line preconcentration–ICP-MS, was adopted previously by our group to determine trace lead in aqueous solutions.[17] Different from a microporous membrane, the Nafion membrane takes advantage of a bonded functional group to selectively absorb polar solvents, which are then removed by air as the sweep gas.[17,21,22] The air cannot diffuse through the wall to cause ICP turbulence.

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Due to success of the proposed method, we extended the application of on-line preconcentration-ICP-MS equipped with the same desolvation unit to concurrently detect ten metal elements including Ni, Zn, Rh, In, Tl, Cu, Ag, Cd, Au, and Pb in aqueous solution and seawater in the present work. Trace-metal complexing with ammonium salt of *O,O*-diethyl dithiophosphate (DDPA) may be retained in a microcolumn packed with C_{18}-bonded silica, followed by elution with methanol into ICP-MS for detection. The standard aqueous solution containing a multi-elemental mixture will be examined with the same operational parameters to determine the corresponding detection limit for each element and the certified reference seawater will finally be applied for detection.

Experimental

ICP-MS apparatus

As in our previous experiments,[17,23-25] an ICP-MS (SCIEX ELAN 6000, Perkin-Elmer, USA) was run in a sequential mode, peak hopping to masses of interest throughout this work. An ultrasonic nebulizer (U-5000 AT, Cetac, USA) served as a sprayer for sample introduction. The coolant gas flow rate, the auxiliary gas flow rate, and the aerosol gas flow rate were fixed at 15.0, 1.0, and 1.05 L/min, respectively, throughout the experiment. The rf power was optimized at 1200 W.

Membrane dryer

As previously reported,[17] a Nafion multi-tube membrane dryer (Perma Pure Co.) was installed behind the ultrasonic nebulizer to further remove the organic solvent from entering the ICP-MS apparatus. With the operation temperature controlled in the range of 90 – 110°C, a maximum desolvation efficiency of about 52% could be achieved. Given an intake speed of methanol of 1.2 mL/min, the desolvation efficiency of the ultrasonic nebulizer could be determined to be 66% with the heating and cooling conditions fixed at 140 and 4°C, respectively.[17] Therefore, the total methanol removal amounted to 83% after installing an ultrasonic nebulizer-Nafion multi-tube membrane
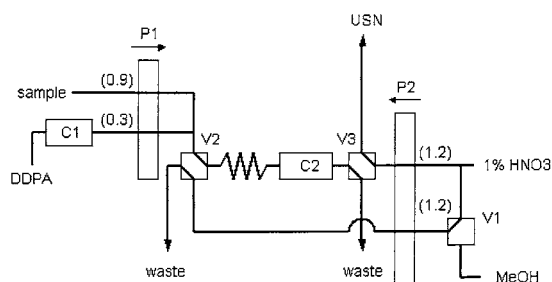
Fig. 1   Schematic diagram of the on-line preconcentration system. P1 and P2, peristaltic pumps; C1, C_{18}-microcolumn for DDPA purification; C2, C_{18}-microcolumn for preconcentration/separation; V1 – V3, solenoid valves; USN, ultrasonic nebulizer. The flow rates (mL/min) for DDPA, sample solution, HNO_3, and methanol are also indicated.
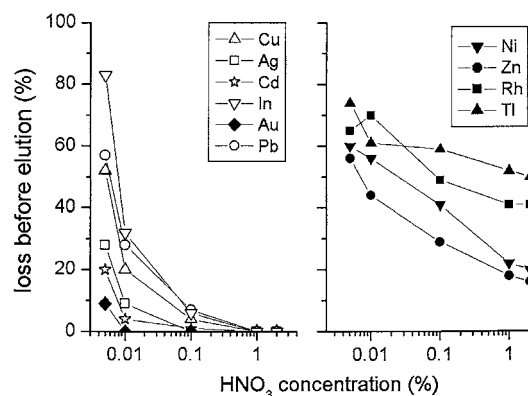

Fig. 2   Loss fraction, for each metal element before eluting with methanol, as a function of the HNO_3 concentration, given a 0.4% DDPA concentration.

desolvator.   Its reliability for a long-working period was inspected by using a Rh sample as a test.

Reagents and DDPA purification

Ten heavy metals including Cd, Ni, Cu, Pb, Zn, Ag, Tl, Rh, Au, and In were selected for the ease for comparison with other techniques. They were mixed with desired amounts in a 1% HNO_3 solution by using individual standard solutions purchased with ICP analytical grade or high-purity standards.   The deionized water was used to prepare solutions.   Reference seawater (NASS-5, National Measurement Standard), with most of the metal elements certified, was acidified to pH 1.6 with HNO_3 prior to examination.

DDPA (reagent grade, 95% purity) was purchased from Aldrich, and then diluted to 0.4% (w/v) concentration in a 1% (v/v) HNO_3 solution.   A large amount of contaminants was found to reside in DDPA before purification.   Elements like Ni, Cu, and Zn were the major contaminants.   A cartridge filled with C_{18}-bonded silica was then used to pre-purify the DDPA reagent.   After 3-min of flowing through the cartridge, the trace metals were significantly reduced.   The pretreated DDPA reagent was further purified through an on-line C_{18}-bonded microcolumn prior to forming a complex with the analytes.

On-line preconcentration operation

As displayed in Fig. 1, the on-line preconcentration system 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, USA), each packed with C_{18}-bonded silica gel. The first microcolumn was used to remove metal contaminants present in DDPA, while the second one was used to preconcentrate the metal samples and to minimize the matrix interference.   The PTFE reaction coil (0.76 mm i.d. and 50 cm long) was knotted to minimize the dispersion of carrier streams and to facilitate the chelating reaction.

A mode of time-limited control was used for sample loading in the manifold.   The metal solution mixture was loaded at a flow rate of 0.9 mL/min for 60 s, while a DDPA solution was flowed at 0.3 mL/min for 60 s.   The metal and DDPA solutions were mixed along a knotted reaction coil and the resultant metal-DDPA complexes were retained in the C_{18}-column.   The complexes were rinsed with a 1% HNO_3 solution at a flow rate of 1.2 mL/min for 40 s to remove excess reagents and matrices, followed by elution with methanol at 1.2 mL/min for 20 s to the ultrasonic nebulizer.   Before loading the next sample, the microcolumn was washed with methanol at 1.2 mL/min for 30

s, and then a 1% HNO_3 solution at 1.2 mL/min for 90 s.

Results and Discussion

Optimization of on-line preconcentration–ICP-MS

The ICP-MS operational conditions were optimized using a sample containing various metal elements, each with 2.0 ng/mL (Ni with 1.0 ng/mL) in a methanol solution.   The rf power dependence of varied metal elements exhibited the same trend with an optimized value at 1200 W.   Nevertheless, the signal-to-background (*S/B*) ratios made a large difference; for instance, the *S/B* ratio for In was 15-times larger than that for Au.   As for the dependence of the aerosol gas-flow rate, the detected *S/B* ratios became very sensitive to this parameter, in contrast to the rf power dependence, which showed a gradual variation.   The optimized value was at 1.05 L/min for all of the metal elements.

The on-line preconcentration conditions were also optimized with the loading of 100 μL of a multi-elemental aqueous solution, including the concentration, pH condition, loading rate of DDPA and the sample, and the methanol elution rate.   The metal *S/B* ratio was measured as a function of one parameter, while the remaining conditions were fixed.[17]   Similar procedures were applied to find the optimal conditions for the other parameters.

Analyte losses prior to elution step

Since identical operation conditions for the on-line preconcentration–ICP-MS were adopted, the difference in the metal-DDPA complexing capacity and the efficiency of complex sorption on the C_{18}-bonded silica may have resulted in losses of the metal contents to some extent prior to methanol elution into ICP-MS.   The losses of metal contents were analyzed in the sample loading and washing steps, during which the four-port valve was switched to ICP-MS.   The loss fraction is defined as the total peak areas before the step of methanol elution divided by those acquired in the whole process.   Given a flow rate of sample solution and DDPA fixed at 0.9 and 0.3 mL/min, respectively, the dependence of the metal losses on the HNO_3 concentration, used in the acidity preparation for the DDPA agent and the sample solution, was characterized.   As shown in Fig. 2, the metal studied may be divided into two groups.   The extent of metal losses for Cu, Ag, Cd, In, Au, and Pb, classified in the first group, were sensitive to the HNO_3 concentration.   For instance, In was found to reach 83% loss

Table 1 Limits of detection for various metal elements detected simultaneously in aqueous solution, and an examination of metal contents in reference seawater (in units of ng/L)

Element	Calibration sensitivity (10^3 count/ppt)	LOD	NASS-5	
			This work	Certified value
^{58}Ni	3.3	20	240 ± 30	253 ± 28
^{63}Cu	3.3	20	290 ± 20	297 ± 46
^{66}Zn	2.9	20	110 ± 20	102 ± 39
^{103}Rh	6.8	3	< LOD	—
^{108}Ag	2.8	4	17 ± 4	—
^{114}Cd	3.5	5	21 ± 5	23 ± 3
^{115}In	9.4	3	< LOD	—
^{197}Au	1.0	4	< LOD	—
^{205}Tl	3.5	5	33 ± 4	—
^{208}Pb	8.6	3	10 ± 4	8 ± 5

with 0.005% HNO_3, and then drop to < 1% loss, when HNO_3 was increased to 1%. The remaining metals (Ni, Zn, Rh, and Tl) were in the second group. Their losses decreased slowly to 18 – 50% with an increase of the HNO_3 concentration up to 1%. The less loss in the early stage certainly resulted in the larger signal intensity detected in the elution step with methanol. These two classes are characterized based on their complexation stability with DDPA.

The DDPA concentration dependence of the metal signal intensity, acquired in the elution step with methanol, was examined for metal loss. The peak area for each metal almost reached a plateau at a high concentration of DDPA. Therefore, 0.4% DDPA was adopted for analysis in aqueous solution and seawater. Other factors, such as the washing time of the complex, the flow rates of DDPA and sample solutions, and the elution speed of methanol, were also characterized for the metal losses. Accordingly, we kept the washing time to be 40 s, the flow rate to be 1.2 mL/min (a sum of 0.3 mL/min DDPA and 0.9 mL/min sample solution), and the elution rate of methanol to be 1.2 mL/min.

Trace metal detection in aqueous solution and seawater

The mixtures, with ten metal elements prepared in identical concentrations of 30, 50, 100, 500, and 1000 ng/L in 1% HNO_3 solutions, were loaded for 60 s. The calibration-curve measurements yielded a linear dynamic range within the concentrations used. The obtained calibration sensitivity for all elements are listed in Table 1. The LOD values, defined as the ratio of three-times the standard deviation (3σ) of the blank measurement to the slope of the calibration curve, were thus determined in the range of 3 – 20 ng/L (ppt) as 0.9 mL of the sample solution loaded (Table 1). The contaminations of Ni, Zn, and Cu existing in the DDPA reagent resulted in a higher LOD for these elements.

As described previously,[17] we used the standard addition method to determine the contents of trace metals in seawater, since these elements are scattered over a wide mass range. Given the conditions optimized for the aqueous solutions, seawater (NASS-5) was loaded at 0.9 mL, and then analyzed. The results, given in Table 1, are in an acceptable range. The values for Rh, In, and Au were under LOD in this work. These elements lack certified values. Tl and Ag were determined to be 33 ± 4 and 17 ± 4 ng/L, respectively, but certified values were not available. Although the metal elements in the second group were less sensitive using the current method, the determined concentrations for Ni and Zn in seawater generally agree with the certified values. Especially for Zn, DDPA was once suggested not to be a suitable complex agent.

As compared to the ion-exchange resin method,[26-28] or an electrothermal vaporization coupled with the on-line preconcentration–ICP-MS apparatus,[29,30] the detection limits for the elements studied in this work were either comparable to or worse than by an order of magnitude. Ion-exchange resins usually require a strong acid mixture as an eluent. Continuously pumping strong acid mixture into the sampler cone might cause some damage, or shorten the lifetime of the apparatus, if without appropriate protection. As for the electrothermal vaporization technique, it requires a skilled person to operate this on-line system. Without running risks, or avoiding the problems described above, this work has demonstrated the sorbent extraction method to be successful for multi-elemental analysis, even with a single kind of sorbent reagent.

Conclusion

Different from our previous work on a single-element detection, we have extended the on-line preconcentration–ICP-MS combined with a desolvation unit for the determination of multi-metal amounts in aqueous solution and seawater. The extent of metal losses prior to the elution step was examined in order to help understand the nature of each complex for optimizing the operational conditions. A detection limit of metals studied from 3 to 20 ng/L could be achieved. If a single element was detected alone, the detection limit could be further improved without making any compromise to optimize the working conditions. Nevertheless, DDPA is not recommended to form the complexes with Cu, Ni, and Zn, since these elements may easily contaminate the reagent from purchase.

Acknowledgements

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