Supplementary Material on the Analytical methods Publication

Amine functionalized polyacrylonitrile fibers for the selective preconcentration of trace metals prior to their on-line determination by ICP-MS

Xiaoyu Jia [a, b,*], Junyi Zhao [a, b], Jiani Wang [a], Hongyun Ren [a], Zixiao Hong [a] and Kun Wu [a, b]

[a] *Key Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, P. R. China*

[b] *ZheJiang Key Laboratory of Urban Environmental Processes and Pollution Control, Ningbo Urban Environment Observation and Research Station, Chinese Academy of Sciences, Ningbo 315830, P.R. China*

**Corresponding author, Tel: +86-574-86085868; Fax: +86-574-86785814*

E-mail: xyjia@iue.ac.cn

The solid phase extraction (SPE) pre-experiment

In this study, 16 trace metal elements included of V(V), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), As(III), Cd(II), Sn(IV), Sb(III), Ba(II), Tl(II), Pb(II) and Bi(II) were used for separation and enrichment procedure. A series of mixed solutions with different concentration gradients (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 μg L^{-1}) were prepared and adsorption experiments were carried out offline. In these metal elements, V(V), As(III), Sn(IV), Sb(III) and Bi(II) can be adsorbed rapidly on the home-made SPE column without any additional reagent. The results showed that, except for these five elements, the adsorption efficiency of other elements are less than 50%, some elements even do not have adsorption action with the fibers.

Effect of sample flow rate

In this work, the influence of the sample flow rate on the adsorption percentage of V(V), As(III), Sn(IV), Sb(III) and Bi(II) were also investigated in the ranges of 1–6 mL min^{-1}, while keeping other conditions constant. The results demonstrated that the adsorption efficiency were almost kept constant till 3 mL min^{-1}, and then it starts to fall with further increase of flow rate, the adsorption equilibrium of metal ions cannot be maintained at too high flow rate, as shown in Fig. S3. Therefore, to ensure adsorption efficiency as well as shorten analysis time, all the experiments at a flow rate of 3 mL min^{-1} were adopted in this study. This good tolerance to the high flow rate is ascribed to the stable mechanical properties of the amine functionalized polyacrylonitrile fibers.

Effect of sample volume

It is also necessary to examine the maximum applicable sample volume especially when the practical samples containing very low level of targets were analyzed. The influence of sample volume on the recoveries of a 0.1 μg L^{-1} mixed standard solution was investigated in the range of 10–50 mL. The results depicted in Fig. S4 shown that the recoveries were found to be stable only till 30 mL, then decreased with further increasing of volume. The reason might be that the active adsorption sites of amine functionalized PANFs are limited, and excessive sample volume may cause elution of some analytes. At last, 30 mL was selected as the final sample volume in this study.

Effect of wash time after extraction

The residual target analytes inside the system especially at the pipeline and interface after extraction will probably interfere the subsequent measurement. Moreover, the complicated matrix in real environmental water samples could cause the instability of the plasma torch, it may be deposited on the sample cone and/or skimmer cone of ICP-MS. Thus, ultrapure water was used to cleaning the system since the metal ions will not be interact with water molecules. The results show that 1 min duration was sufficient to completely remove the residue with negligible effect on the next analytical run at a flow rate of 3 mL min^{-1}.

Optimization of the eluent type and flow rate

According to the coordination adsorption mechanism and chemical properties of metal ions, a certain concentration acid solution was selected to elute metal ions. According to subsequent detection methods, HNO_3 were chosen as eluent, while phosphates and chlorides were not adopted in order to avoid interference. Thus, different concentration gradients containing of 0.1, 0.2, 0.3, 0.4, 0.5 mol L^{-1} nitric acid were used as eluent, respectively. The elution efficiency gradually increased with the increase of HNO_3 concentration to medium concentration, after that no obvious change was observed. Because excessive levels of acid may cause damage to the adsorbent materials as well as bring a higher background to the method, 0.3 mol L^{-1} HNO_3 solution was adopted in this work, while higher concentrations were not recommended.

Eluent flow rate is one of the most important parameters need to be optimized. Since the method of on-line elution was used here, the analytes were directly eluted via a U3000 pump and determined by ICP-MS. In order to match the flow rate of ICP-MS nebulizer and avoid the instability of plasma torch, too high elution rate is not recommended. For this purpose, 0.5, 0.8, 1.0 and 1.5 mL min^{-1} was adopted to perform the experiment. When the flow rate is lower than 1 ml $\min^{-1}$, the elution efficiency does not change too much, however, when the flow rate is higher than 1 ml $\min^{-1}$, the torch was unstable and the discharge of ICP-MS waste was not smooth. Thus, the flow rate of 1 ml $\min^{-1}$ was used for elution in this study.

Optimization the determination conditions

For the determination of V(V) and As(III), double charged interference of $^{36}Ar^{12}C$, $^{35}Cl^{16}O$, $^{40}Ar^{12}C$ and $^{40}Ar^{35}Cl$ existed particularly for real samples analysis that may cause an increased background and reduce sensitivity. Consequently, kinetic energy discrimination (KED) model was adopted for interference elimination, the only parameter here that needs to be optimized is the flow rate of helium gas. Thus, the flow rate for He was studied in the range of 3-5 mL $\min^{-1}$, and the results showed that 4.516 mL $\min^{-1}$ was operative for reducing the background from 4000 cps to fewer than 100 cps. In addition, high sensitivity of Co (Co/ClO>18) as well as good stability of internal standard were obtained.

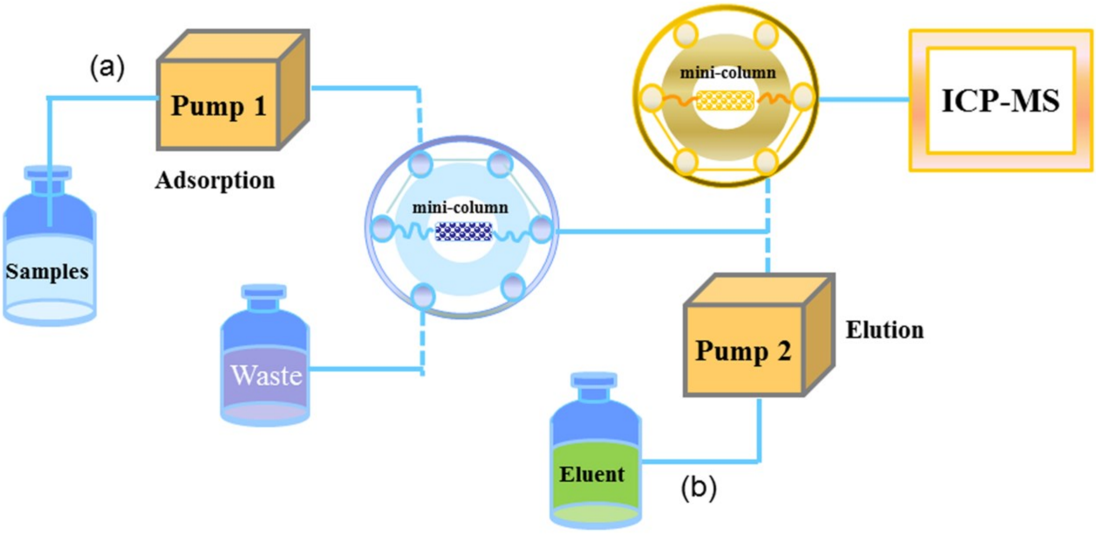

Fig. S1 Schematic representation of the on-line SPE–ICP-MS system

(a) Filling of the sample onto the mini-column (b) Elution of the trace metal ions.

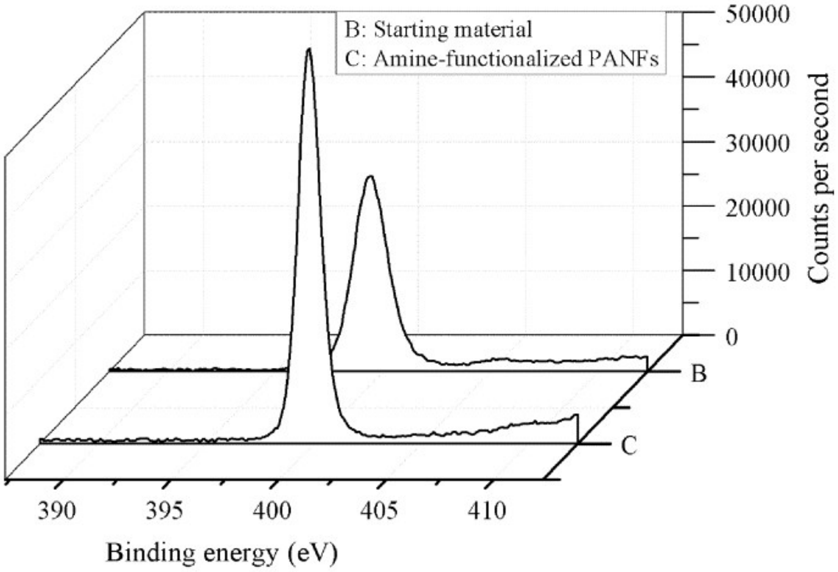

Fig. S2 Comparison of the XRF spectrum (B) Starting material (C) Amine-functionalized PANFs

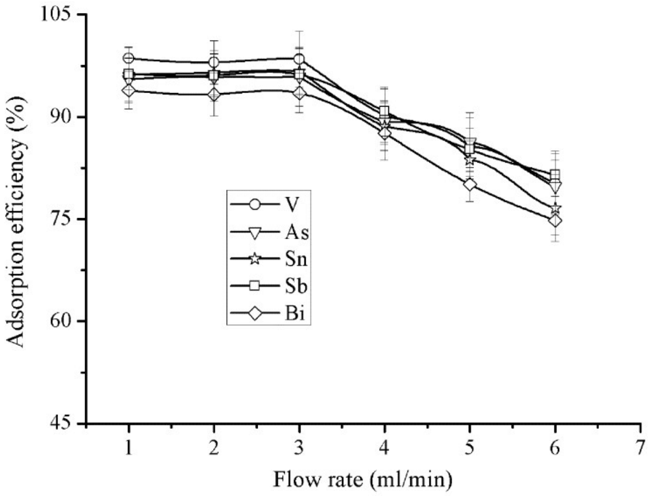

Fig. S3 Effect of flow rate on the adsorption efficiency of trace metals.

Concentration: 0.1 µg L^{-1}, Sample volume: 30 mL, pH 7.

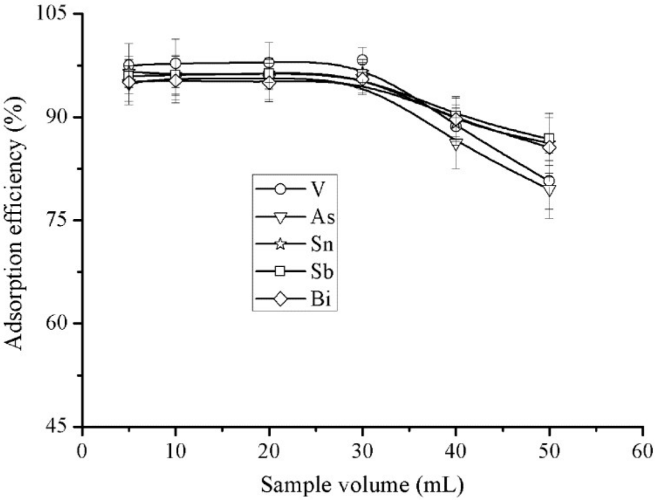

Fig. S4 Effect of sample volume on the adsorption efficiency of trace metals.

Concentration: 0.1 µg L^{-1}, flow rate: 3 mL min^{-1}, pH 7.

Table S1 Optimized experimental parameters of ICP-MS and U3000

Parameters	Value
ICP-MS system	1550
RF power (W)	
Nebulizer gas flow (L min^{-1})	1.05
Auxiliary gas flow (L min^{-1})	0.80
Cooling gas flow (L min^{-1})	14.0
Extraction Lens 2 (V)	–105.3
CCT Focus Lens (V)	–11.60
Sampling cone (mm)	1.0, Ni cone
Skimmer cone (mm)	0.5, Ni cone
Isotopes monitored	^{51}V, ^{75}As, ^{118}Sn, ^{121}Sb, ^{209}Bi
Dwell time (ms)	30
Acquisition mode	Peak jumping
Collision gas (He, mL min^{-1})	4.516
Resolution	Normal
U3000 system	
Elution	0.3 mol L^{-1} HNO_3
Flow rate	1.0 mL min^{-1}
Sample loop	Mini-column (30 mm×4.6 mm)

Table S2 Analytical results and recoveries of trace metals in three water samples

Water sample	Trace metals	Concentration (μg L^{-1}) Mean ± S.D.[a]	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Lake water	V	0.377 ± 0.005	0.500	0.864 ± 0.006	98.5
	As	0.106 ± 0.002	0.100	0.211 ± 0.002	102
	Sn	0.213 ± 0.004	0.500	0.709 ± 0.007	99.4
	Sb	0.359 ± 0.003	0.500	0.851 ± 0.005	99.0
	Bi	0.483 ± 0.005	0.500	0.995 ± 0.008	101
River water	V	0.326 ± 0.005	0.500	0.813 ± 0.005	98.4
	As	0.237 ± 0.001	0.200	0.435 ± 0.003	99.5
	Sn	0.460 ± 0.004	0.500	0.953 ± 0.010	99.3
	Sb	0.353 ± 0.002	0.500	0.846 ± 0.006	99.2
	Bi	0.464 ± 0.003	0.500	0.979 ± 0.007	102
Sea water	V	0.392 ± 0.003	0.500	0.883 ± 0.005	99.0
	As	0.613 ± 0.002	0.500	1.105 ± 0.006	99.3
	Sn	0.479 ± 0.005	0.500	0.971 ± 0.007	99.2
	Sb	0.325 ± 0.002	0.500	0.821 ± 0.005	99.5
	Bi	0.926 ± 0.003	1.000	1.945 ± 0.006	101

[a] Standard deviation ($n = 3$).