



Separation and determination of colloidal trace metals in seawater by cross-flow ultrafiltration, liquid-liquid extraction and ICP-MS

Yuxi Lu^{a,b}, Xuelu Gao^{a,b,*}, Chen-Tung Arthur Chen^c

^a CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, Shandong 264003, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Department of Oceanography, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

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ABSTRACT

In this study, a method was developed for the desalination and pre-concentration of three colloidal trace metals in seawater, namely Cd, Cu and Pb, using diethylammonium diethyldithiocarbamate and ammonium 1-pyrrolidine dithiocarbamate as chelates. Seawater samples were first treated with cross-flow ultrafiltration (CFUF) for the separation of the colloidal matter of different molecular weights, i.e. 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μm . Then, after acid digestion, the organic chelates and the extracting agent chloroform were added at pH = 3.8. Finally, the organic phase was back extracted, and the target metals in all samples were measured using inductively coupled plasma mass spectrometry (ICP-MS) with low detection limits in the range of 0.13–1.18 pmol L^{-1} . The extraction efficiencies for the three metals were in the range of 92.2%–100.3% with an enrichment factor of 40, and their mass recoveries in the studied colloidal fractions were in the range of 83.1%–103.5%. The developed method has been successfully applied for the analysis of seawater samples collected from the sites off the south coast of North Yellow Sea in Shandong Peninsula, China. For the first time, the distribution of colloidal Cd, Cu and Pb in different molecular weights in this area is reported. The results obtained from real samples demonstrate that the developed method is simple, efficient and convenient for routine analysis with low detection limit.

1. Introduction

Aquatic colloids are known to be abundant and conventionally defined as nanoparticles and macromolecules with the size ranging from 1 nm to 1 μm (Gustafsson and Gschwend, 1997; Guo and Santschi, 2007; Santschi, 2018). In environmental studies, 0.45 μm filters are typically used to separate the water into particles and dissolved phases, ignoring the presence of colloids (Waeles et al., 2008; Gu et al., 2013), which led to limited research in this field. The colloids in water bodies are unstable and susceptible to changes in microtopography, polymerization, and sedimentation. In addition, due to their high molecular weight and large specific surface area, the reactive functional groups attached to the surface of colloids can strongly adsorb and complex with nutrients, trace metals and various organic contaminants in aquatic environments (Buffle, 2006; Hochella et al., 2008; Auffan et al., 2009). As is known, the ions of some metals such as Cd, Cu and Pb are toxic and could have serious harmful effects on life over certain

concentrations (Manju et al., 2015). The functional groups of colloids, such as carboxyl groups, hydroxyl groups and amino groups, have strong adsorption and complexing ability with metal ions in water body, which can significantly affect their solubility, migration, sedimentation, bioavailability and toxicity. Meanwhile, studies have found that high molecular weight organic matter in colloids is easily absorbed by microorganisms (Amon and Benner, 1996). Coastal seas are a vast sink of anthropogenic contaminants, and they are also the place where people farm to get seafood (Huang et al., 2013). Trace metals in coastal seas, especially those with high toxic effects on living organisms, can be enriched through the food chain and eventually reach higher concentrations, threatening human health. However, due to a lack of efficient and clean pretreatment methods, high quality data on the publication of colloidal metals in the coastal waters of China are scarce. Therefore, it is of great significance to develop an efficient separation and determination method to study the biogeochemistry of trace metals in various phases of water bodies (Um and Papelis, 2002; Huang et al.,

* Corresponding author at: CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, Shandong 264003, China.

E-mail address: xlgaoy@yic.ac.cn (X. Gao).

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2015; Markus et al., 2018).

Cross-flow ultrafiltration (CFUF), a commonly used colloidal separation technique, can separate colloids from aquatic systems based on their molecular weight or size in environmental research (Powell et al., 1996; Liu et al., 2013). The application of CFUF in the study of aquatic systems, especially that of the distribution of metals between the colloidal phase, e.g. the dissolved matter of > 1 kDa, and the truly dissolved phase, e.g. the dissolved matter of < 1 kDa, provides valuable information on the biogeochemistry of trace elements in aquatic systems (Guo et al., 2007; Gu et al., 2013). In comparison with other separation techniques, CFUF can process quickly large volumes of water samples, which can ensure more subsequent research (Pokrovsky et al., 2012; Huang et al., 2014). However, after seawater sample was ultrafiltered, the retentate and ultrafiltrate contain high concentrations of sodium chloride, which will interfere with the signal value of the target element in the subsequent analysis (Biparva and Matin, 2012; Liu et al., 2018). Meanwhile, for some metals with lower concentration, such as Cd and Pb, contamination may occur during the collection and routine instrument analysis, which may result in the final measured concentration being higher than the true value (Li et al., 2015). Thus, it is necessary to select an appropriate pretreatment method, e.g. liquid-liquid extraction, to enrich the colloidal trace metals separated after CFUF processing. By this approach, the concentration of trace metals can be concentrated, and in addition, the effect of high concentration of sodium chloride on the detection results can be eliminated and the accuracy of the results can be guaranteed.

In this study, for the first time, we combined a liquid-liquid extraction method with CFUF and ICP-MS, and successfully detected colloidal trace metals of different molecular weights, i.e. 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μm , in the coastal waters of Shandong Peninsula, North Yellow Sea (NYS), China. Diethylammonium diethyldithiocarbamate (DDDC) and ammonium 1-pyrrolidine dithiocarbamate (APDC) were used as the chelates in the applied liquid-liquid extraction by referencing Li et al. (2015). The application of clean colloidal trace metal separation and determination techniques ensures good accuracy, low detection limits and high recovery of spiked samples. In addition, the data demonstrate the feasibility of the developed method and the reliability of the data. The distributions of the target metals in the colloidal fractions with different molecular weight ranges in the study area are discussed.

2. Experiment and methods

2.1. Reagents

The mixed standard solutions for the three target elements (Cd, Cu and Pb, 1000 mg L^{-1}) were purchased from General Research Institute for Nonferrous Metals (China). APDC (Guaranteed reagent) was purchased from Aladdin Industrial Corporation (Shanghai, China), and DDDC (Guaranteed reagent) was supplied by TCI Chemical Industry Co., Ltd. (Shanghai, China). The concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) were obtained by re-distilling trace metal grade HNO_3 (Sinopharm Chemical Reagent Co., Ltd., China) and HCl (Sinopharm Chemical Reagent Co., Ltd., China) with a sub-boiling distillation apparatus (BSB-939-IR, Berghof, Germany). The polypropylene sampling bottles (Thermo®) were pre-cleaned following a cleaning process modified from Li et al. (2015), i.e. first cleaned with 10% Decon 90™ (Decon Laboratories Ltd., UK), and then sonicated successively in 1.5 mol L^{-1} HNO_3 , 1.2 mol L^{-1} HCl, and ultra-pure deionized water (DIW; 18.2 $\text{M}\Omega\text{-cm}$) for 3 h. The DIW used in this work was made by a Pall Cascada™ lab water purification system (Pall Corporation). Each sampling bottle was double bagged in polyethylene bags, and stored at 20–25 °C for further use. All the experimental labware used in this study was also pre-cleaned following the above cleaning process and dried in a Class 100 clean bench. The experimental operations were also carried out in the clean bench at ~25 °C.

2.2. Sampling

Field samples used in this study were surface seawater (1–2 m deep) collected from 2 sites off the north coast of Shandong Peninsula, the NYS, in May and September 2018, respectively (Supplementary Material Fig. S1). Site Y1 was located in the Sishili Bay, a busy region in the south coast of the NYS, which is greatly affected by aquaculture and human activities (Zhang et al., 2016); site Y2 was located in the Rongcheng Bay, a fast-growing aquaculture area, which was an important part of the Shandong Peninsula Blue Economic Zone in the national development strategy of China (Yang et al., 2001; Huang et al., 2013). Samples were collected in pre-cleaned polypropylene bottles that had been flushed in the field with seawater. Then in the laboratory, the samples were filtered through Supor®-200 0.22 μm membrane filters (Pall Corporation) and collected in pre-cleaned 4 L polypropylene bottles and then stored at 4 °C before further processing. In order to ensure the accuracy of the experimental results, the sampled seawater was filtered within 4 h (Waeles et al., 2008; Xu et al., 2018).

2.3. Cross-flow ultrafiltration

Millipore Prep/scale™ devices with regenerated cellulose membranes of 1, 3 and 10 kDa nominal pore size, respectively, were set up for the size fractionation of water samples. The schematic diagram of the CFUF system is shown in Supplementary Material Fig. S2. Before each experiment, the CFUF system was pre-cleaned using the method reported in Guo and Santschi (1997). Briefly, the entire CFUF system, including membrane and C-flex® tubing (Cole-Parmer Inc.), was first cleaned with 2 L of 1% Micro-90 detergent and then recirculated with 0.2 mol L^{-1} NaOH, 0.2 mol L^{-1} HCl and DIW for 50 min, respectively, to remove possible contamination. Finally, the system was rinsed with 1 L of seawater sample before CFUF. In short, 10 L of seawater pre-filtered with 0.22 μm filters were sequentially passed through three CFUF systems with 10, 3 and 1 kDa molecular weight cutoffs, respectively, using a peristaltic pump (Masterflex® L/S, Cole-Parmer Inc.), and the permeate flow with the matter less than the molecular weight cutoff of the CFUF membrane was directed into a permeation reservoir (Reservoir 2, Supplementary Material Fig. S2) until the concentration factor (*cf*) reached around 15–20. The flow rate during rinsing and CFUF was 30–40 mL min^{-1} . After the CFUF treatment, the colloidal matter with > 1 kDa molecular weight was significantly concentrated in the retentate reservoir (Reservoir 1, Supplementary Material Fig. S2).

As an important parameter affecting the CFUF efficiency, *cf* can be used to describe the dynamic relationship between retentate volume and prefiltrate volume at any given time of ultrafiltration (Logan and Jiang, 1990). In previous studies, different *cf* was applied to the study of colloidal matter. For example, Wen et al. (1996) used a macromolecular permeation model based on Kilduff and Weber (1992) to study colloidal metals in the Galveston Bay with a *cf* of about 10. Liu et al. (2013) used a larger *cf* of ~17 in the study of colloidal matter in some selected UK freshwaters. While in the study reported by Liu and Lead (2006), the reliable determination of colloidal components required a *cf* of 15–20 in a research on the Vale Lake and Tern River, UK. Therefore, this range was used as the *cf* throughout the present study.

2.4. Liquid-liquid extraction

To reduce the saline interference and enrich the target metals at the same time, we used a liquid-liquid extraction method reported in Li et al. (2015) to treat all tested samples, including the samples after CFUF separation, and the experiments were carried out in triplicate for every experimental condition.

Briefly, 400 mL of acidified seawater or colloidal samples were transferred into a Teflon separation funnel, then 5 mL of pH 3.8 acetic acid-ammonium acetate buffer and 1.5 mL of superior grade ethanol solution containing 0.05 mol L^{-1} APDC and 0.04 mol L^{-1} DDDC were

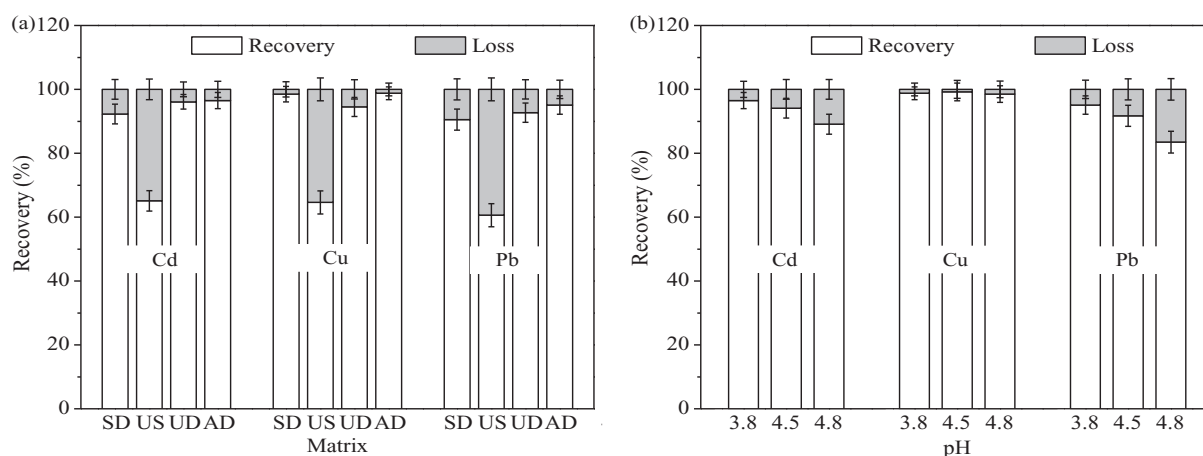


Fig. 1. Recoveries of Cd, Cu and Pb extraction in different matrices (a) and at different pH conditions (b). SD: spiked DIW; US: undigested seawater; UD: UV-digested seawater; AD: acid-digested seawater.

added. The solution was then extracted with 5 mL chloroform 3 times and shaken for 1 min each time. Then, after separated from the extraction apparatus, the obtained chloroform phases were finally combined and 500 μ L of concentrated HCl and 500 μ L of concentrated HNO₃ were pipetted to the chloroform phase to back-extract the target metals. The acid phase was pipetted into a pre-cleaned 15 mL centrifuge tube, then placed in a clean bench and left uncovered for 2 h for the evaporation of the remaining chloroform. Finally, 0.5 mL of the acid phase was then pipetted into another pre-cleaned 15 mL centrifuge tube and diluted to 5.0 mL with 0.5 mol L⁻¹ HNO₃. The application of this method eliminated the possible interference of salt matrix and chloroform during instrumental analysis and concentrated the metals in each of the 3 colloidal fractions with the molecular weight ranges of 1–3 kDa, 3–10 kDa and 10 kDa–0.2 μ m obtained by CFUF for 40 times.

2.5. Trace metal analysis and data processing

In general, when the retentate, permeate, total dissolved concentration and *cf* are known, colloidal metal concentrations can be calculated by difference (Buesseler et al., 1996). Therefore, after the necessary pretreatment, the pre-filtered seawater (< 0.22 μ m), ultrafiltrate and retentate samples were measured using an inductively coupled plasma mass spectrometer (ICP-MS, ELAN DRC II, PerkinElmer®), and the concentration of each colloidal trace metal (1–3 kDa, 3–10 kDa and 10 kDa–0.22 μ m) was calculated according to the following formula reported in Fu et al. (2011):

$$C_{C1K} = (C_{R1K} - C_{TD}) cf1$$

$$C_{C3K} = (C_{R3K} - C_{C1K} - C_{TD}) cf2$$

$$C_{C10K} = (C_{R10K} - C_{C3K} - C_{C1K} - C_{TD}) cf3$$

in which, C_{TD} is the concentration of truly dissolved phase (< 1 kDa); *cf1*, *cf2* and *cf3* are the concentration factors (i.e. the volume of pre-filtrate divided by the volume of retentate), which are stabilized at about 17 in this study; C_{C1K} , C_{C3K} and C_{C10K} are the concentration of colloidal metals of 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μ m, respectively; C_{R1K} , C_{R3K} and C_{R10K} are the metal concentrations in the 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μ m retentates, respectively.

After the determination of every 12 samples, a mixed standard solution of target trace metals (8.9 nmol L⁻¹ Cd, 15.7 nmol L⁻¹ Cu and 4.8 nmol L⁻¹ Pb) in 1 mol L⁻¹ HNO₃ was run on the ICP-MS as the quality control (Liu et al., 2018). The instrumental baseline was corrected by running the 1 mol L⁻¹ HNO₃ to determine the instrument blank after every 12 injections.

3. Results and discussion

3.1. Effects of the sample digestion method

Complex matrices in seawater significantly affect the bonding between various metals and organic and inorganic ligands (Colombo et al., 2008). Previous studies have found that the dissolved organic matter (DOM) in aquatic system could significantly affect the behavior of metals (Turner et al., 2008; Cobelo-García, 2013). Therefore, the binding of DOM to metal in the sample must be removed before subsequent processing to minimize its impact on the experimental results.

In this research, the samples were pretreated with ultraviolet irradiation (Achterberg et al., 2001) and acid digestion (Li et al., 2015), which are two main methods for removing DOM from seawater, to determine the effects of the two pretreatment methods on the liquid-liquid extraction rate. Briefly, in the UV irradiation process, seawater samples were irradiated under a 500 W high pressure mercury lamp (emission wavelength: 356 nm, Model: GGZ500, Shanghai Jiguang Special Lighting Appliance Factory, China) for over 48 h until the concentration of background DOC was < 0.01 mg L⁻¹ measured by a Shimadzu TOC-V_{CPH} carbon analyzer (Japan), which was consistent with corresponding result in Liu et al. (2018). The UV irradiation chamber was a 1 L quartz tank covered with a quartz cover embedded in a lid. The distance between the mercury lamp (in the middle of the chamber) and the sample was about 2 cm. Concentrated HNO₃ was added to the seawater sample to make its pH stable at 1.8 in the acid digestion process. In addition, for comparison, extraction experiments of Cd, Cu and Pb in undigested natural seawater and spiked DIW were also carried out simultaneously. The spiked Cd, Cu and Pb levels of the four pretreatment methods were 8.9, 15.7 and 4.8 nmol L⁻¹, respectively.

As shown in Fig. 1a, various recovery efficiencies could be found for different matrices and metals, and high extraction efficiencies were obtained in both acid-digested and UV-digested samples. In contrast, however, the acid-digestion method had the advantage of the extraction efficiencies for Cu and Pb. The extraction rate of the undigested sample was < 65.1% for all the three metals, indicating that organic matter in seawater could significantly reduce the extraction efficiency. In addition, similar recoveries of Cd, Cu and Pb were obtained in the acid-digested sample and the spiked ultrapure water sample (Fig. 1a). Although UV digestion also has a good performance in terms of extraction efficiencies, considering the operation time, the acid digestion method was selected for the digestion of the samples.

3.2. pH conditions

As an important factor, pH could significantly affect the binding

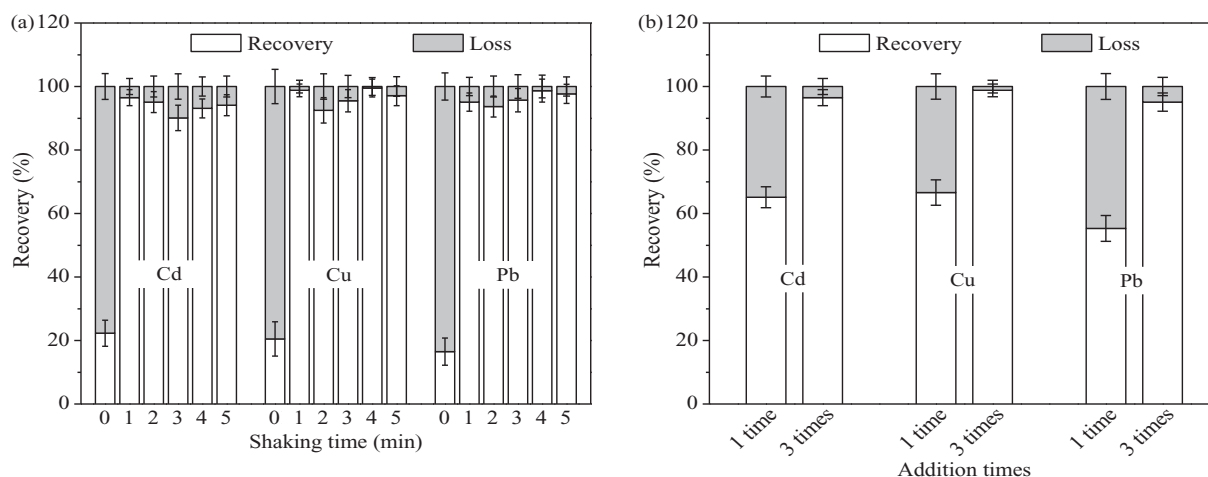


Fig. 2. Recoveries of Cd, Cu and Pb extraction at different shaking time (a) and in different addition times (b). The spiked Cd, Cu and Pb levels of the two spiking experiments were 8.9, 15.7 and 4.8 nmol L⁻¹, respectively.

efficiency of organic chelates to trace elements (Pinto et al., 2015). Some studies have demonstrated that APDC and DDDC have excellent binding capabilities for many elements over a wide pH range of 2.5–5.5 (Bruland et al., 1979; Su et al., 2006; Wang and Wang, 2014). Therefore, we chose the acetic acid-ammonium acetate as the buffer in the extraction process, and three pH values, namely 3.8, 4.5 and 4.8, were tested for the selection of the appropriate pH. The standard solution with 8.9 nmol L⁻¹ Cd, 15.7 nmol L⁻¹ Cu and 4.8 nmol L⁻¹ Pb was added to the acid digested seawater samples collected from site Y1 before they were subjected to the 3 parallel liquid-liquid extractions. The background values of three metals in the unspiked seawater were detected before calculating the final recovery.

As shown in Fig. 1b, it could be seen that these elements have different binding abilities to organic matter within this pH range. The recovery of Cd decreased significantly from 96.5% at pH = 3.8 to 89.1% at pH = 4.8. Similar to that of Cd, the recovery of Pb decreased from 95.1% to 83.5% with the increase in pH from 3.8 to 4.8. The recovery of Cu was relatively stable and > 98% at each tested pH value. Thus, we chose 3.8 as the optimum pH condition for the extraction process.

3.3. Effects of the sample volume

Due to the generally low concentration of Cd, Cu and Pb in natural seawater (Srichandan et al., 2016; AlSuhaimi et al., 2017), improving the extraction efficiency can be achieved by increasing the enrichment factor. However, if the sample volume was too large during the experiment, the extraction time would be prolonged with the increasing amounts of the reagent, and a better extraction effect could not be necessarily obtained. On the contrary, if the sample volume was too small, it would be difficult to obtain the expected degree of enrichment and the accuracy of the experimental results would be affected. Therefore, 200 and 400 mL were selected as the experimental sample volumes to search the optimal sample volume for liquid-liquid extraction. In short, after the seawater was ultrafiltered through the 10 kDa, 3 kDa and 1 kDa CFUF devices, 200 and 400 mL of each of the < 1 kDa, 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μm fractions were taken for enrichment, respectively. All fractions were treated repeatedly for 3 times, and then they were determined using ICP-MS to get the extraction efficiencies. Finally, the extraction efficiencies of the three metals for each of the sample volumes were compared. The results showed that the extraction efficiencies of the three elements for the 200 mL sample volume were 97.0% for Cd, 97.4% for Cu and 96.0% for Pb, and the corresponding values for the 400 mL sample volume were 95.3% for Cd, 98.8% for Cu and 95.1% for Pb, which means there was no significant

difference. However, when the sample volume was 400 mL, the enrichment factor could reach 40 and was higher than that of the 200 mL sample volume, which has certain advantages in the operation. Moreover, the concentrations of the target metals in each of the subsamples were lower than their originals after separation by the CFUF system. Therefore, 400 mL was selected as the actual sample volume in the liquid-liquid extraction processing.

3.4. Effects of the shaking time in extraction

In the extraction process, when the time spent on shaking is insufficient, the target elements could not be effectively extracted. Conversely, it is inefficient and unnecessary to shake for a longer time when ideal extraction efficiency is achieved. Hence, six periods of shaking time spanned from 0 to 5 min with an increment of 1 min were tested for the selection of the proper one while the other experimental conditions were kept unchanged. Start shaking when chloroform was added to the solutions. 0 min means that no shaking operation was made, and chloroform settled to the bottom of the solutions under gravity. 3 parallel experiments were treated for each shaking time, and then they were determined using ICP-MS.

As shown in Fig. 2a, the extraction efficiencies of the three elements were 22.3% for Cd, 20.5% for Cu and 16.5% for Pb when no shaking operation was made. When the shaking time was 1–5 min, the extraction rate was basically stable at above 90%, which indicated that 1 min is enough and the extension of shaking time has little benefit for getting a higher extraction rate (Fig. 2a). This may be due to the fact that, after entering the aqueous phase, the organic phase disperses evenly and rapidly due to the action of the oscillation, and the system quickly reaches the extraction equilibrium (Sorouraddin et al., 2017). In order to minimize the extraction time and ensure a high extraction rate, we chose 1 min as the shaking time in extraction.

3.5. Effects of the extractant volume and extraction method

Besides by the methods of increasing the enrichment factor, a higher extraction rate could also be achieved by the selection of an appropriate extractant volume or adding method (Costa et al., 2018). In previous studies, 14–15 mL chloroform was added as the extractant (Bruland et al., 1979; Li et al., 2015). Bruland et al. (1979) used 14 mL chloroform, which was added in two portions with 6 and 8 mL, to extract trace metals in 250 g seawater samples, and good recoveries were gained. Li et al. (2015) used 15 mL chloroform, which was added three times with 5 mL each time, to extract trace metals in 200 g seawater samples. Considering the larger sample volume (400 mL) in this study compared

to the 200–250 g in Bruland et al. (1979) and Li et al. (2015), 15 mL of chloroform were added all at once and in three portions with 5 mL each time to compare the extraction efficiencies of the three metals. After adding chloroform, the system was shaken for 1 min. For the three-time addition experiments, the extractants were collected and mixed together, and then subjected to further processing.

As shown in Fig. 2b, although the one-time addition method could simplify the experimental operation process and shorten the pretreatment time, the recoveries of Cd, Cu and Pb it got were all lower than 70%, especially for Pb, which was only 55.3%. For the three-time addition method, the recoveries of Cd, Cu and Pb were 96.5%, 98.8% and 95.1%, respectively. Although the extraction time was prolonged, ideal extraction rates could be guaranteed using the three-time addition method. Therefore, adding 5 mL chloroform each time for 3 times was applied in this research.

3.6. Method validation

3.6.1. Detection limit (LOD) and quantification limit (LOQ)

The working solutions were prepared by diluting Cd, Cu and Pb standard solution. Under the optimal ICP-MS conditions, the six-point calibration curves of the three metals, established by the relationships between their corresponding spectral line intensities and the concentrations, were obtained. The method blank, as an important indicator of analytical experiment, mainly involved two parts. One was the system blank, caused by the filters, CFUF membranes, piping, glassware and plasticware during the extraction operation as well as the instrument used. The other was the reagent blank, which was caused by the reagents used in the experiment such as DIW, re-distilled HNO₃, HCl, buffer, organic chelates and chloroform. In this study, the blank samples were treated repeatedly for 11 times using the developed method, and then they were determined using ICP-MS to get the blank values. The detection limits (LOD) for the target elements were assessed at 3 times of the standard deviation (σ) of the blank values, and the quantification limits (LOQ) were calculated based on 10σ . The performance of the developed method is shown in Table 1.

Lower LOD and LOQ were significant guarantees for the accuracy of the experimental results (Luan et al., 2017). The linear ranges of the three metals were 0.2–444.8 nmol L⁻¹ Cd, 1.6–786.8 nmol L⁻¹ Cu and 0.5–241.3 nmol L⁻¹ Pb, respectively. As for LOD, Cd and Cu were 0.68 and 1.18 pmol L⁻¹, respectively; the value of Pb was relatively low, approaching 0.13 pmol L⁻¹; for LOQ, all three metals were below 3.92 pmol L⁻¹. In summary, LOD and LOQ of the developed method can meet the requirements of daily experiments.

3.6.2. Extraction rate

In order to test the extraction efficiency of the method, certain concentrations of Cd, Cu and Pb standard solutions were added to the acid digested seawater collected from site Y1, then it was subjected repeatedly for 11 times to liquid-liquid extraction at the optimum conditions selected in Sections 3.1–3.5, and after that it was determined by ICP-MS. The results showed that the measured values of Cd, Cu and Pb in the sample were quite consistent with the theoretical values, and the extraction rate was 92.2–100.3% (Fig. 3a).

For Cd and Pb, during the entire experimental process, the adsorption of the vessels, the residues in the extraction and back

extraction operations, etc., will cause metal loss and reduce the extraction efficiency. Therefore, it is necessary to select an extraction system and containers with a low adsorption effect (Cobelo-García et al., 2007). For Cu, the extraction rate was slightly > 100%. Therefore, the experimental process must be ensured by using high purity reagents, applying clean operation technique and reducing system errors. Overall, the results showed that the method used in this study had satisfactory extraction efficiency and could reach the requirement of enrichment of trace metals in seawater.

3.6.3. Recoveries of CFUFs

Good mass balance is a key factor for ensuring the performance of the entire CFUF system, as that described in Liu and Lead (2006) and Liu et al. (2007). In this research, mass balance was performed by the adding of known amounts of Cd, Cu and Pb standard solutions into the 0.22 μ m filtered seawater samples from site Y1. After being successively processed by CFUFs with 10, 3 and 1 kDa molecular weight cutoffs and the other necessary pre-processing, the concentrations of the three metals were obtained by 3 parallel determinations of ICP-MS under the optimal determination conditions. The mass balance recoveries of the three metals were calculated based on a reported formula expressed as the following form (Liu et al., 2013):

$$\text{Recovery} = 100\%(C_p V_p + C_r V_r)/C_i V_i$$

in which, C_p , C_r and C_i represent permeate, retentate and initial concentrations, and V_p , V_r and V_i represent permeate, retentate and initial volumes. If a recovery value is > 100%, it means that the researched component is contaminated during CFUF processing; if a recovery value is < 100%, there is a loss of the researched component in the CFUF process (Chen et al., 2000).

As shown in Fig. 3b–d, the results showed that the recoveries of the methods at the three different spike levels were between 83.1% and 103.5%, indicating that the developed method can be applied in the separation and determination of the three colloidal metals in real seawater samples. At the same time, it should be noted that a thorough cleaning process is necessary and indispensable for improving the efficiency of the entire CFUF system and the accuracy of the experiment (Guo and Santschi, 2007).

3.6.4. Method application for actual seawater samples

To evaluate the applicability, the proposed method was used in the analysis of the studied trace metals in the surface seawater of two sites, namely site Y1 and Y2 in Fig. S1. Using the colloidal separation method described in Section 2.3, the colloidal matter in seawater with 1–3 kDa, 3–10 kDa, and 10 kDa–0.22 μ m molecular weights were gained. The fraction that can pass through the 1 kDa CFUF membrane was defined as the truly dissolved phase. After ultrafiltration, the pH of the samples was adjusted to 1.8 by concentrated HNO₃. Then, the trace metals were enriched by the enrichment method described in Section 2.5. Finally, the samples were determined for target metals by ICP-MS.

The results showed that there was an obvious difference in both concentrations and percentages of the dissolved metals in each CFUF cutoff range at sites Y1 and Y2. In terms of concentrations, as shown in Fig. 4a, Cd, Cu and Pb at site Y1 were 0.061, 2.03 and 1.52 nmol L⁻¹ in the 1–3 kDa fraction, 0.024, 1.02 and 1.23 nmol L⁻¹ in the 3–10 kDa fraction, and 0.012, 2.30 and 1.35 nmol L⁻¹ in the 10 kDa–0.22 μ m fraction, respectively; at site Y2, their corresponding values were 0.0087, 2.32 and 1.91 nmol L⁻¹ in the 1–3 kDa fraction, 0.017, 1.83 and 3.17 nmol L⁻¹ in the 3–10 kDa fraction, and 0.012, 1.04 and 3.12 nmol L⁻¹ in the 10 kDa–0.22 μ m fraction. This obvious difference between the two sites could be attributed to spatial/temporal variations and the result of many complex biogeochemical interactions. Meanwhile, the addition of large amounts of feed and drugs during aquaculture can easily cause the accumulation of heavy metals in water bodies and sediments (Mendiguchia et al., 2006), which may be a main reason for the high Pb level at site Y2.

Table 1
Performance of the developed method.

	Cd	Cu	Pb
Linear ranges (nmol L ⁻¹)	0.2–444.8	1.6–786.8	0.5–241.3
Detection limit (pmol L ⁻¹)	0.68	1.18	0.13
Quantification limit (pmol L ⁻¹)	2.25	3.92	0.42
Enrichment factor of liquid-liquid extraction	40	40	40

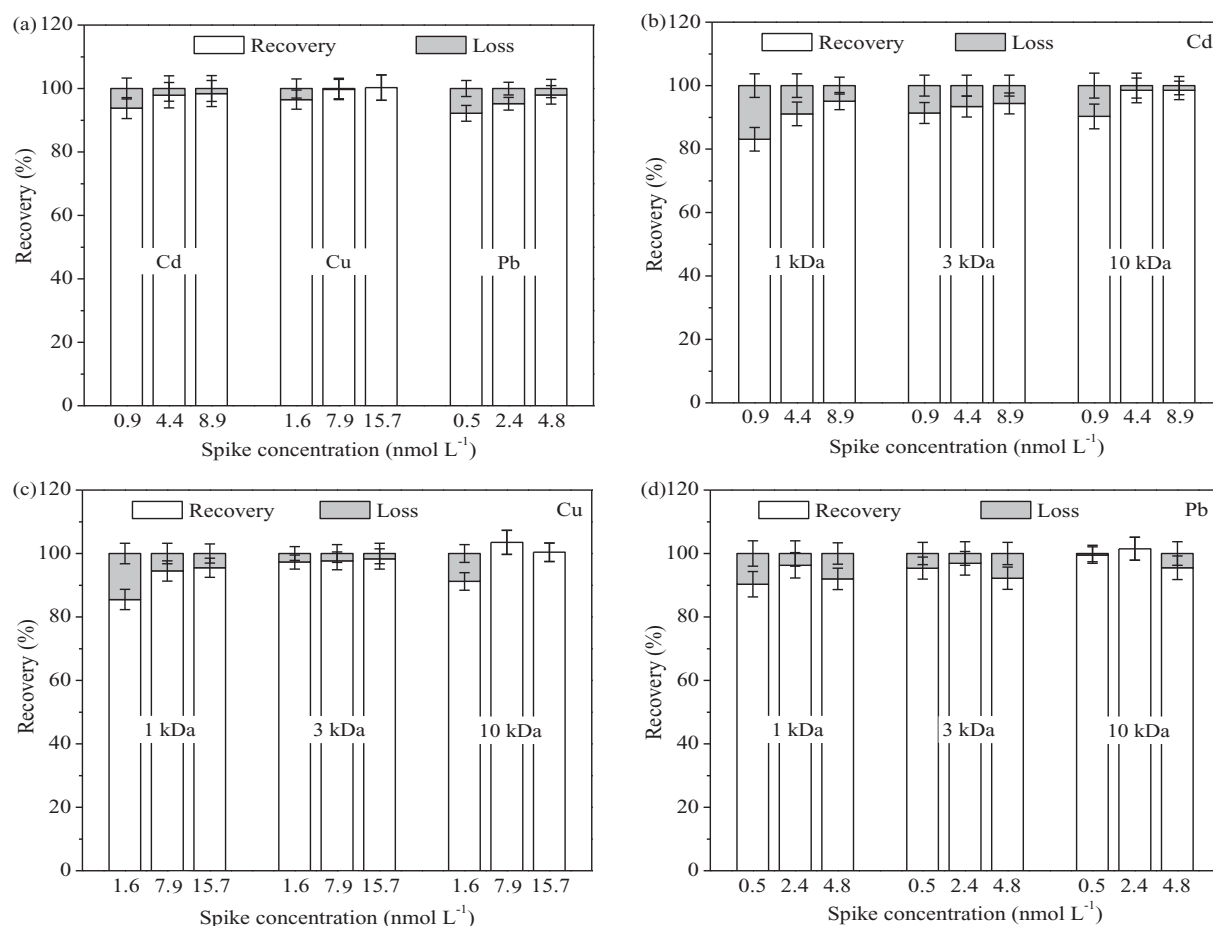


Fig. 3. Recoveries of Cd, Cu and Pb in different spike concentrations (a) and in different nominal pore size of CFUF systems (b, c and d).

However, the percentage distribution of the three metals among the colloidal phases (1 kDa–0.22 μ m) and the truly dissolved phase (< 1 kDa) still had some regularity. As it can be seen from Fig. 4b, colloidal Cd and Pb at site Y1 and colloidal Cd and Cu at site Y2 had similar values in percentage terms, which accounted for 47–51% of the total dissolved pool; colloidal Cu at site Y1 and colloidal Pb at site Y2 also had similar values in percentage terms, which accounted for 31% of the total dissolved pool. At site Y1, the 1–3 kDa fraction of Cd, Cu and Pb accounted for 30%, 12% and 19% of their respective total dissolved concentrations, the 3–10 kDa fraction of Cd, Cu and Pb accounted for

12%, 6% and 15% of their respective total dissolved concentrations, and the 10 kDa–0.22 μ m fraction of Cd, Cu and Pb accounted for 6%, 13% and 16% of their respective total dissolved concentrations; at site Y2, the corresponding values of colloidal Cd, Cu and Pb were 12%, 23% and 7% in the 1–3 kDa fraction, 23%, 18% and 12% in the 3–10 kDa fraction, and 15%, 10% and 12% in the 10 kDa–0.22 μ m fraction. Therefore, for the colloidal fractions, these three metals were more likely to bind to the dissolved organic matter with 1–10 kDa molecular weight, indicating that the colloidal matter of this molecular weight range may play an important role in their biogeochemical cycles, which

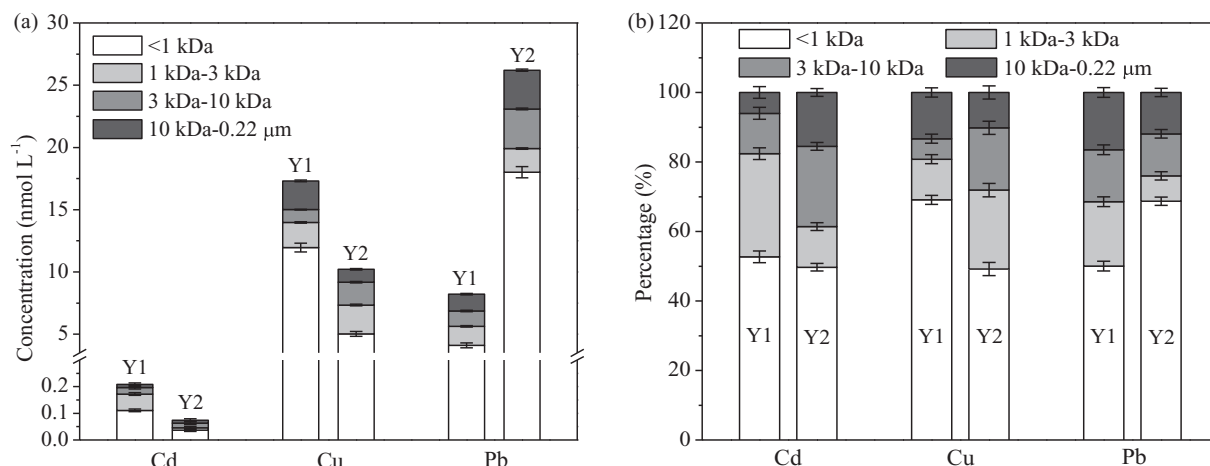


Fig. 4. Concentration and percentage distribution of Cd, Cu and Pb in the dissolved fractions of samples collected in the North Yellow Sea.

Table 2
A comparison of the data in this study and the other literature. C_{TD} and C_C represent the concentrations of truly dissolved phase and colloidal phase, respectively.

Location	Prefilter (μm)	Membrane's cutoff (kDa)	Concentration factor	C_{TD} (nmol L^{-1})			C_C (nmol L^{-1})			$C_C/(C_{TD} + C_C)$ (%)			Reference
				Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb	
Coastal water of NYS (site Y1), China	0.45	1, 3 and 10	~17	0.11	11.96	4.11	0.098	5.35	2.75	47	31	50	This study
Coastal water of NYS (site Y2), China	0.45	1, 3 and 10	~17	0.037	5.03	18.01	0.037	5.19	8.20	50	51	31	This study
Venice Lagoon, Italy	0.4	10^a	~1.1	0.0070–0.083	3.15–8.85	0.021–0.16	0.0010–0.043	1.18–8.34	0.0020–0.98	34	41	58	Martin and Dai (1995)
Lake Taihu, China	1	1	^b	0.011–0.13	23.92–50.99	37.50–103.19	0.060–0.16	7.24–13.53	12.64–17.86	59	22	21	Zhang et al. (2007)

^a 10 kDa was used as the boundary between colloidal and truly dissolved phases in that study.

^b “.” represents no relevant reference data.

is similar to the previous report by Wen et al. (1999). Typically, organic matter with 1–10 kDa molecular weight range are primarily considered to be humic/fulvic compounds or newly released peptides such as polypeptides (Lead and Wilkinson, 2006; Kawakami et al., 2006). In addition, the degradation of particulate organic matter or the particle desorption may significantly affect the migration of the metals (Gobeil et al., 1987; Gerringa et al., 1996). Obviously, the sources of organic matter are rich and its supply is abundant in the coastal and aquaculture areas, especially estuaries.

As shown in Table 2, in comparison to other aquatic environments, the colloidal Cd in percentage terms in the coastal waters of the Shandong Peninsula was close to that of the Lake Taihu (59%), but higher than that of the Venice Lagoon (34%); the proportion of colloidal Pb to its value in the total dissolved pool was lower than that of the Venice Lagoon (58%) (Martin and Dai, 1995), but higher than that of the Lake Taihu (21%) (Zhang et al., 2007). In terms of concentration, colloidal Cd in this study was 0.037 and 0.098 nmol L^{-1} , and colloidal Cu was 5.19 and 5.35 nmol L^{-1} , both lower than that of the Lake Taihu, but higher than that of the Venice Lagoon; colloidal Pb was 2.75 and 8.20 nmol L^{-1} , which was close to that of the Lake Taihu (12.64–17.86 nmol L^{-1}), but still higher than that of the Venice Lagoon (0.0019–0.97 nmol L^{-1}).

Overall, the concentration of colloidal trace metals varied widely, and this phenomenon may be due to the specific properties of metals and the nature of different aquatic systems (Ingri et al., 2004). Furthermore, colloidal metals still occupy a large proportion of their total dissolved pool, which is a significant part of studying the trace metal geochemical cycle and its environmental significance (Ran et al., 2000; Singhal et al., 2006; Pourret et al., 2007). However, for a single element, it can be found that the total dissolved concentration may not play a critical role in regulating the interaction of the truly dissolved phase and each colloidal fraction. In other words, a high total dissolved concentration does not necessarily lead to an increase in the concentration of colloidal phase or each colloidal fraction, e.g. 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μm , and the main factors affecting the migration of various metal elements remain to be further studied. Meanwhile, due to the lack of data on the spatiotemporal distribution and variation of colloidal trace metals in the NYS, there is no comparison and discussion of their monthly, seasonal or annual changes in this study.

4. Conclusions

A rapid, effective and sensitive method has been developed for the separation and determination of three colloidal trace metals including Cd, Cu and Pb in seawater. The method provided lower detection limit and good accuracy. Excellent recoveries were successfully obtained, which was about 83.1%–103.5%. Meanwhile, the use of the developed method allowed the effect of salt matrix to be effectively removed. The method achieved a high enrichment factor of 40, which made the separation and determination of colloidal metals in seawater more efficient.

After using this method for the analysis of the coastal waters of the Shandong Peninsula, it could be found that Cd, Cu and Pb in the colloidal phase accounted for 31–51% of the total dissolved pool. In addition, the 1–10 kDa may be the key fraction of the migration process for Cd, Cu and Pb in coastal ecosystem, and the main factor affecting the migration of trace metals among the fractions with different molecular weight range, e.g. < 1 kDa, 1–3 kDa, 3–10 kDa and 10 kDa–0.22 μm , may not be simply the change of their total dissolved concentration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marchem.2019.103685>.

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