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# Simultaneous and selective preconcentration of trace Cu and Ag by one-step displacement cloud point extraction for FAAS determination

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ABSTRACT

A simple, rapid and selective one-step displacement cloud point extraction (D-CPE) procedure was developed for the simultaneous preconcentration of trace Cu and Ag followed by flame atomic absorption spectrometric (FAAS) measurement. In this proposed procedure, Ni–DDTC complex instead of DDTC was used to achieve one-step extraction. Since the stability of Cu–DDTC and Ag–DDTC is higher than that of Ni–DDTC, simultaneous preconcentration of Cu and Ag can be achieved in a single step. Up to 15,000 mg L$^{-1}$ Co$^{2+}$, 10,000 mg L$^{-1}$ Zn$^{2+}$, 5000 mg L$^{-1}$ Cd$^{2+}$ and 5000 mg L$^{-1}$ Al$^{3+}$ did not cause significant interferences for the determination of 50 μg L$^{-1}$ Cu by FAAS, while 8000 mg L$^{-1}$ Zn$^{2+}$, 4000 mg L$^{-1}$ Co$^{2+}$, 4000 mg L$^{-1}$ Cd$^{2+}$ and 5000 mg L$^{-1}$ Al$^{3+}$ had no distinct effect on the determination of 80 μg L$^{-1}$ Ag. The limits of detection (LODs) of 0.5 μg L$^{-1}$ for Cu and 1.0 μg L$^{-1}$ for Ag, respectively, were obtained by FAAS detection. The accuracy of the proposed method is validated by analyzing certified reference materials (GBW 07405, GBW 07311 and GBW 07260) with satisfactory results. Furthermore, the one-step D-CPE was also applied for the preconcentration/separation of Cu and Ag in high-purity salts and artificial seawater, followed by FAAS or inductively coupled plasma-mass spectrometry (ICP-MS) determination.

## 1. Introduction

Sample preparation is often regarded as the Achilles' heels of an analytical method, as analytes of interest in some cases are extremely low in concentration and/or co-existed with complex sample matrix. Accurate analyte quantification thus requires efficient matrix elimination and analyte preconcentration prior to eventual various instrumental measurements. Methods for sample preparation are often described in the literature [1,2], including conventional schemes, such as liquid–liquid extraction (LLE) [3,4] and solid-phase extraction (SPE) [5,6], and a lot of new approaches, for example, solid-phase microextraction (SPME) [7,8], liquid–liquid microextraction (LLME) [9,10], single drop microextraction [11], cloud point extraction (CPE) [12–14], and ionic liquid extraction [15]. In most cases, the whole analytical procedure is desired to be simple, efficient, sensitive, and selective.

Recently, a highly selective displacement sorption preconcentration protocol has been developed by Yan and co-workers [16–18] for the determination of analytes in complicated matrices. Later, Christou took the advantage of on-line displacement/solid-phase extraction system for the selective determination of Ag in water samples [19]. The main principle of this technique was based on the fact that interested metal (M1) with higher complex (M1-L, L is the ligand) stability can take the place of another metal (M2) with lower complex (M2-L) stability from its complex. Through the displacement reaction, interferences from co-existing ions were greatly eliminated and efficient analyte preconcentration can be achieved simultaneously. Enlightened by Yan's displacement sorption, we have previously designed a displacement cloud point extraction (D-CPE) procedure for the determination of Ag in soil and ore samples [20]. The previous D-CPE procedure involved two CPE steps: the first step for the extraction of Cu–DDTC (diethyldithiocarbamate) and the second one for Ag displacement of Cu from Cu–DDTC. Although efficient matrix elimination was achieved, two steps CPE involved in D-CPE procedure made the whole procedure time- and labor-consuming.

Due to fast formation kinetics of metal–DDTC complex, it was expected that the previously reported D-CPE can be further simplified to one single step via properly controlling the sequence of reagent addition. Also, an extraction scheme for simultaneous and selective preconcentration of several metals can be easily achieved because DDTC is a versatile metal chelating reagent. Therefore, in this work, a one-step D-CPE protocol was proposed for the simultaneous preconcentration of trace elements (with Cu and Ag as models) from complicated matrices (e.g. soils, artificial seawater and high-purity salts) and the subsequent determination by flame atomic absorption spectrometry (FAAS) or inductively coupled

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**Table 1**
Instrumental operating parameters for FAAS and ICP-MS.

| Parameters | Settings | |
|---|---|---|
| FAAS | | |
| Element | Cu | Ag |
| Absorption line (nm) | 324.7 | 328.1 |
| Lamp current (mA) | 4 | 5 |
| Atomizer height (mm) | 7 | 7 |
| Flow rate of acetylene ($\mathrm{L\,min^{-1}}$) | 1.5 | 1.8 |
| Flow rate of air ($\mathrm{L\,min^{-1}}$) | 8.0 | 8.0 |
| Spectral bandwidth (nm) | 0.2 | 0.4 |
| ICP-MS | | |
| RF power (W) | 1150 | |
| Plasma gas flow ($\mathrm{L\,min^{-1}}$) | 15 | |
| Auxiliary gas flow ($\mathrm{L\,min^{-1}}$) | 1.20 | |
| Nebulizer gas flow ($\mathrm{L\,min^{-1}}$) | 0.93 | |
| Lens voltage (V) | 6.50 | |
| Isotope monitored | $^{63}$Cu, $^{107}$Ag | |

plasma-mass spectrometry (ICP-MS). Compared with the previous D-CPE [20], the current one-step D-CPE is of simplicity and rapidity, without sacrifice of selectivity.

## 2. Experimental

### 2.1. Instrumentation

A GGX-6 polarized Zeeman flame atomic absorption spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was used for the atomic absorbance measurements for Cu and Ag. A Model ELAN DRC-e ICP-MS instrument (Perkin Elmer SCIEX) was also employed to determine the trace Cu and Ag in analytical reagents and seawater. The major instrumental parameters for the FAAS and ICP-MS measurements are summarized in Table 1.

### 2.2. Reagents

All reagents used were of at least analytical grade. Stock standard solutions of 1000 $\mathrm{mg\,L^{-1}}$ $\mathrm{Cu^{2+}}$ and $\mathrm{Ni^{2+}}$ were carefully prepared by dissolving CuO and NiO (spectral purity grade) in 2% (v/v) $\mathrm{HNO_3}$, respectively. The standard stock solution of 100 $\mathrm{mg\,L^{-1}}$ $\mathrm{Ag^{+}}$ was purchased from the National Research Center for Standard Materials (NRCSM) of China. Working standard solutions were prepared by serial dilution of the stock standard solutions with double distilled water (DDW). The chelating reagent was prepared by dissolving DDTC in DDW with a final DDTC concentration of $1 \times 10^{-2}$ $\mathrm{mol\,L^{-1}}$. The non-ionic surfactant Triton X-114 purchased from Fluka was used in this work. The desired pH of the solutions was adjusted by using 0.2 $\mathrm{mol\,L^{-1}}$ sodium acetate (NaAc) and 0.1 $\mathrm{mol\,L^{-1}}$ NaOH.

### 2.3. Operating procedure

The one-step D-CPE for FAAS involved the following steps: first, $\mathrm{Ni^{2+}}$ and DDTC were mixed to form Ni–DDTC in a 10 mL centrifuge tube with a final concentration of 30 $\mathrm{mg\,L^{-1}}$ and $4.0 \times 10^{-4}$ $\mathrm{mol\,L^{-1}}$ for $\mathrm{Ni^{2+}}$ and DDTC, respectively; second, a solution containing Cu, Ag and 0.20% Triton X-114 was added, and 0.2 $\mathrm{mol\,L^{-1}}$ NaAc was used to adjust the pH to 5.0; and last, DDW was used to dilute the solution to the 10 mL mark. It is vital that $\mathrm{Ni^{2+}}$ and DDTC should be added firstly to form the Ni–DDTC complex, otherwise co-existing metal ions in samples would compete for DDTC with $\mathrm{Ni^{2+}}$ and analytes; and as a result, the displacement reaction between co-existing metal ion, $\mathrm{Ni^{2+}}$ and analytes would make the whole process time-consuming. The solution containing analyte was heated in the water bath at 30 °C for 5 min. Separation of the phases was achieved by centrifugation at 3200 rpm for 10 min. After carefully removing aqueous phase by syringe, the surfactant-rich phase containing Cu–DDTC, Ag–DDTC and Ni–DDTC complexes was diluted with a solution containing 10% $\mathrm{HNO_3}$ (v/v) and 20% methanol (v/v) to 400 μL before FAAS determination. For the ICP-MS measurements, the concentration of Ni–DDTC was just one-twentieth of that used in FAAS and other extraction conditions were consistent with those of FAAS determination.

### 2.4. Samples and sample pretreatment

Three kinds of certified reference materials, soil, marine sediment and Ag ore, were analyzed to evaluate the accuracy of this method. A sample of 200 mg was weighed into a high pressure Teflon vessel and a small amount of DDW was added to wet the sample, followed by 9 mL concentrated $\mathrm{HNO_3}$, 3 mL HF and 2 mL concentrated HCl. Then the Teflon vessel was closed tightly and put into the microwave cavity for digestion. The heating program was 320 W for 2 min, 480 W for 2 min, 600 W for 2 min and 800 W for 10 min. After cooling to the ambient temperature, the digest was evaporated to near dryness in a Teflon vial on a hot plate. The moist residue was dissolved in diluted $\mathrm{HNO_3}$ and transferred into a 50 mL volumetric flask and then diluted to the mark. A blank was also prepared in a similar way without the sample.

Three samples of analytical reagents $\mathrm{Co(NO_3)_2{\cdot}6H_2O}$, $\mathrm{Zn(NO_3)_2{\cdot}6H_2O}$ and $\mathrm{CdCl_2{\cdot}6H_2O}$ of higher than 99.0% purity were weighted (1, 1 and 0.5 g) and dissolved with distilled water, and then transferred into 50 mL flasks with final concentrations of 20, 20 and 10 $\mathrm{g\,L^{-1}}$, respectively.

The artificial seawater was prepared according to Chamsaz' work [21]. The composition of artificial seawater included NaCl, 0.4266 $\mathrm{mol\,kg^{-1}}$; $\mathrm{Na_2SO_4}$, 0.0292 $\mathrm{mol\,kg^{-1}}$; KCl, 0.0105 $\mathrm{mol\,kg^{-1}}$; $\mathrm{CaCl_2}$, 0.0107 $\mathrm{mol\,kg^{-1}}$; and $\mathrm{MgCl_2}$, 0.0551 $\mathrm{mol\,kg^{-1}}$.

## 3. Results and discussion

### 3.1. Design of one-step D-CPE for simultaneous extraction of Cu and Ag

The displacement sorption preconcentration developed by Yan and Christou [16–19] and our previously reported D-CPE [20] were based on the fact that the stability constants of metal–DDTC complexes decreased in the following order: Hg(II) > Pd(II) > Ag(I) > Cu(II) > Tl(III) > Ni(II) > Bi(III) > Pb(II) > Co(III) > Co(II) > Cd(II) > Tl(I) > Zn(II) > In(III) > Sb(III) > Fe(III) > Te(IV) > Mn(III) > Mn(II). The first step of our previously reported D-CPE was to extract the substrate for the subsequent displacement reaction [20]. In fact, the formation kinetics of metal–DDTC complex is very fast, and thus the required metal–DDTC complex can be obtained by simply mixing the metal ion and DDTC just prior to the addition of the analyte. Hence, the formerly developed dual-step D-CPE can be handled in a single step, when metal–DDTC complex, instead of DDTC, was used as the chelating agent. Additionally, it can be seen from the stability sequence of metal–DDTC complex that great potential for simultaneous preconcentration of at least two metals exists, and we take Cu and Ag as the model elements for this study. In the current one-step D-CPE procedure for Cu and Ag, Tl(III)–DDTC is thought to be the best choice to achieve the best selectivity. However, considering the high toxicity of Tl, Ni–DDTC complex was selected for use. In this case, only $\mathrm{Hg^{2+}}$, $\mathrm{Pd^{2+}}$, $\mathrm{Ag^{+}}$, $\mathrm{Cu^{2+}}$ and $\mathrm{Tl^{3+}}$ can displace $\mathrm{Ni^{2+}}$ from Ni–DDTC complex due to their higher DDTC complex stability. Therefore, the interferences from other co-existing metal ions were largely alleviated. Generally, the concentrations of Hg, Pd, and Tl in many types of samples are usually very low so that the effects of these ions can be ignored.

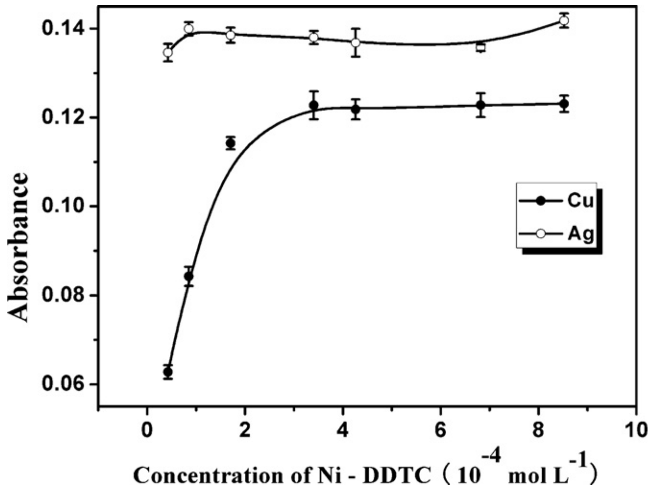

**Fig. 1.** The influence of Ni–DDTC concentration on the preconcentration of 50 μg $L^{-1}$ Cu and 100 μg $L^{-1}$ Ag. Other experimental conditions: Ni–DDTC complex concentration, $4.0 \times 10^{-4}$ mol $L^{-1}$; pH, 5.0; and Triton X-114 concentration, 0.2% (v/v).

### 3.2. Optimization of the extraction conditions

#### 3.2.1. Ni–DDTC concentration

It is well-known that DDTC is prone to complex with transition metal ions at the concentration ratio of 2:1, so this ratio was maintained for the formation of Ni–DDTC in this work. The concentration of Ni–DDTC has a direct influence on the displacement reaction between the analyte and Ni–DDTC, and the subsequent preconcentration procedure. As shown in Fig. 1, Cu (50 μg $L^{-1}$) signal increased sharply with the Ni–DDTC concentration in the range of 0.43–3.4 × $10^{-4}$ mol $L^{-1}$, and then leveled off; while the Ag signal remained almost unchanged. In order to achieve effective preconcentration and reduce the introduction of organic substances into ICP, $4.0 \times 10^{-4}$ mol $L^{-1}$ Ni–DDTC was selected for further experiments.

In order to guarantee the selective extraction and to decrease the amount of free DDTC caused by the complex equilibrium between $Ni^{2+}$ and DDTC, some excess amount of $Ni^{2+}$ was further added before sample introduction. The effect of extra $Ni^{2+}$ concentration was studied and finally 30 mg $L^{-1}$ $Ni^{2+}$ was chosen for use.

#### 3.2.2. pH

In D-CPE, pH is one of the most significant factors affecting the formation of Ni–DDTC complex, the displacement reaction between Cu, Ag and Ni–DDTC, as well as the subsequent extraction efficiency. Fig. 2 shows the effect of pH on the D-CPE efficiencies of Cu and Ag in the pH range of 2.2–8.6. The recovery for Cu increased with increasing pH from 2.2 to 6.0, and reached a maximum at pH 6.0. While the extraction efficiency of Ag increased up to pH 5.0 and almost remained constant in the range of pH 5.0–8.6. At low pH, the low recoveries for both Cu and Ag were probably due to the decomposition of DDTC in acidic medium to liberate $CS_2$. When sample pH is higher than 7, the hydrolysis of metal ions could be a problem. In consideration of all these factors, pH 5.0 (NaAc buffer) was chosen for use in this work.

#### 3.2.3. Concentration of Triton X-114

The effect of non-ionic surfactant concentration was studied and the results are shown in Fig. 3. Maximum absorption signals for Ag and Cu were found at the concentration of 0.2% (m/V). When the surfactant concentration was less than 0.2%, the extraction efficiency was low probably because the surfactant molecule population was not large enough to entrap the DDTC complexes effectively. The decreased absorption signal at the concentrations of surfactant higher than 0.2% was due to the low preconcentration factor and the low efficiency of pneumatic nebulization caused by the increased surfactant volume and large viscosity of the surfactant-rich phase, respectively. Therefore, 0.2% Triton X-114 was selected for use.

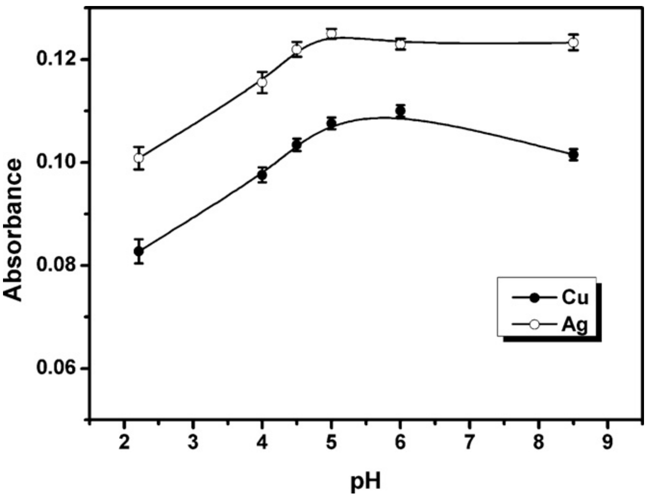

**Fig. 2.** The influence of pH on the preconcentration of 50 μg $L^{-1}$ Cu and 100 μg $L^{-1}$ Ag. Other experimental conditions: Ni–DDTC complex concentration, $4.0 \times 10^{-4}$ mol $L^{-1}$; $Ni^{2+}$ concentration, 30 mg $L^{-1}$; and Triton X-114 concentration, 0.2% (v/v).

#### 3.2.4. Other experimental conditions

In order to achieve quantitative extraction, other experimental conditions, such as equilibration temperature and incubation time, were investigated. Finally, the selected temperature and incubation time were 30 °C and 5 min, respectively. Under the optimized conditions, the two phases can be easily separated by centrifugation at 3200 rpm for 10 min. To decrease the viscosity, 10% $HNO_3$ (v/v) and 20% methanol (v/v) was used to dilute the surfactant-rich phase to 400 μL prior to the instrumental measurements.

### 3.3. Interference study

To demonstrate the superior selectivity of the proposed method, the potential interference from co-exist ions was carefully inves-

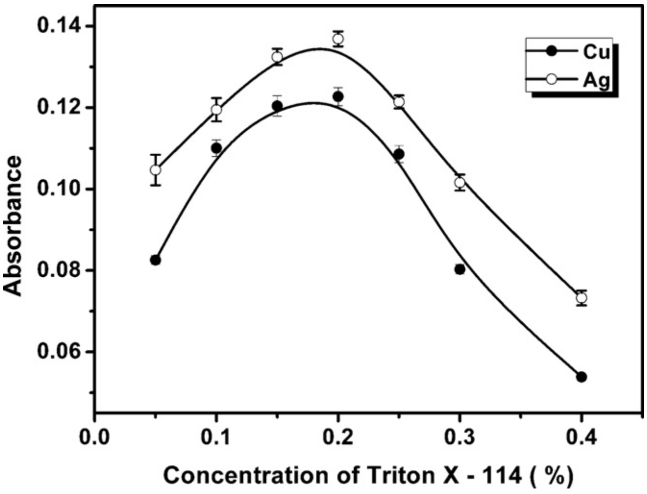

**Fig. 3.** The influence of the concentration of Triton X-114 on the preconcentration of 50 μg $L^{-1}$ Cu and 100 μg $L^{-1}$ Ag. Other experimental conditions: Ni–DDTC concentration, $4.0 \times 10^{-4}$ mol $L^{-1}$; $Ni^{2+}$ concentration, 30 mg $L^{-1}$; and pH, 5.0.

**Table 2**
Investigation of interferences from co-existing metal ions for the determination of 50 μg L$^{-1}$ Cu and 80 μg L$^{-1}$ Ag by using one-step D-CPE preconcentration followed by FAAS determination.

| Ion | Concentration (mg L$^{-1}$) | Ag, recovery (%) | Cu, recovery (%) |
|---|---|---|---|
| Ag(I) | 5 | – | 101 |
| Cu(II) | 2.5 | 95 | – |
| Zn(II) | 8000 | 101 | – |
| | 10,000 | – | 101 |
| Pd(II) | 1 | 92 | 93 |
| Mn(II) | 2000 | 104 | 105 |
| Fe(III) | 50 | – | 106 |
| | 80 | 102 | – |
| Cd(II) | 4000 | 102 | 96 |
| | 5000 | – | 95 |
| Co(II) | 4000 | 103 | – |
| | 15,000 | – | 101 |
| Pb(II) | 1200 | 96 | – |
| | 2000 | – | 107 |
| Hg(II) | 2.5 | 97 | 95 |
| K(I) | 5000 | 94 | 95 |
| Ca(II) | 2000 | 103 | 99 |
| Mg(II) | 2000 | 99 | 97 |
| Al(III) | 5000 | 96 | 94 |
| Na(I) | 5000 | 106 | 98 |

tigated with 50 μg L$^{-1}$ Cu and 80 μg L$^{-1}$ Ag, respectively. The investigation of interferences with the determination of Cu and Ag arising from other interfering species in the one-step D-CPE was tabulated in Table 2. The proposed one-step D-CPE tolerates considerably higher amounts of interfering ions, because these interfering ions with lower DDTC complex stability cannot displace $Ni^{2+}$ from Ni–DDTC complex and can be removed finally. Although relatively low tolerant limits for the co-existing ions $Hg^{2+}$ and $Pd^{2+}$, their concentrations are usually at the trace levels in many types of samples. Therefore, Ag and Cu could be simultaneously and selectively preconcentrated and determined in complicated matrix samples or in pure reagents by using the proposed analytical method.

### *3.4. Analytical characteristics and potential applications*

Under the optimal conditions, the analytical performance of the proposed method was investigated. The sensitivity enhancement factors were 22 for Cu and 24 for Ag, respectively, which are defined as the slope ratio of the calibration curves obtained with D-CPE and without CPE. Linear ranges were obtained over the range of 5–300 and 5–450 μg L$^{-1}$ with a correlation coefficient of 0.9982 and 0.9992 for Cu and Ag, respectively. The limits of detection (LODs, 3$\sigma$) were 0.5 μg L$^{-1}$ for Cu and 1 μg L$^{-1}$ for Ag. The precision of the one-step D-CPE procedure was found to be 2.7% for Cu (50 μg L$^{-1}$, $n = 7$) and 2.6% for Ag (100 μg L$^{-1}$, $n = 7$).

**Table 3**
Analytical results for trace Cu and Ag in certified reference materials by D-CPE FAAS (μg/g).

| Samples | Found[a] (μg/g) | | Certified (μg/g) | |
|---|---|---|---|---|
| | Cu | Ag | Cu | Ag |
| GBW-07405 | 141 ± 3 | 4.6 ± 0.4 | 144 ± 6 | 4.4 ± 0.4 |
| GBW-07311 | 79 ± 2 | 3.2 ± 0.2 | 79 ± 3 | 3.3 ± 0.4 |
| GBW-07260 | 181 ± 4 | 736 ± 10 | 185 ± 6[b] | 732 ± 10 |

[a] Average ± one standard deviation of three trials.
[b] Determined by ICP-MS.

To evaluate the accuracy of the proposed method, several certified reference materials (soil, marine sediment and ore) were analyzed for trace Cu and Ag, and the analytical results were listed in Table 3. A *t*-test shows that the analytical results by the proposed method have no significant difference from the certified values at the confidence level of 95%. The macro-matrix components of these samples, including K, Na, Ca, Mg, Al, and Fe, are in the concentration range of 0.3–10%, while other trace metals, including Ni, Mn, Co, Zn, Pb, and Cr, are in the range of 10–2000 μg/g. These data clearly show the complicated matrices of the selected samples and the high selectivity of the proposed method.

In order to fully verify the applicability of the proposed method toward samples with complicated sample matrices, we attempted to analyze trace impurities in high-purity materials. Currently, there are a lot of reports in the literature on the analysis of high-purity reagents. However, developing a general simple method is still desired as the reported methods are limited for a specified element [22–24] or need expensive high-resolution ICP-MS [25]. When the characteristics of the target analytes are similar to the bulk matrix, the separation of analyte will be even more problematic. Besides, the subsequent cleaning of ICP-MS sampling cone is a tedious but indispensable step to make ready for further measurements. In the current study, we chose to analyze several analytical grade reagents, including $Co(NO_3)_2$, $Zn(NO_3)_2$ and $CdCl_2$ to further verify the accuracy of the proposed method. The results for spiked-recoveries of Cu and Ag in these samples and an artificial seawater

**Table 4**
Analytical results for trace Cu and Ag in high pure reagents and artificial seawater by the proposed method.

| Sample | Added (μg/g) | | Found (μg/g)[a] | | | |
|---|---|---|---|---|---|---|
| | Cu | Ag | FAAS | | ICP-MS | |
| | | | Cu | Ag | Cu | Ag |
| $Co(NO_3)_2$ | 0 | 0 | nd | nd | – | – |
| | 2 | 2 | 2.25 ± 0.15 | 2.20 ± 0.30 | 112%[b] | 110%[b] |
| $Zn(NO_3)_2$ | 0 | 0 | 1.80 ± 0.25 | nd | 1.60 ± 0.15 | 0.031 ± 0.003 |
| | 0.5 | 0.5 | – | – | 1.98 ± 0.12 | 0.605 ± 0.075 |
| | 2 | 2 | 3.69 ± 0.30 | 2.03 ± 0.17 | 94.5%[b] | 102%[b] |
| $CdCl_2$ | 0 | 0 | nd | nd | nd | nd |
| | 2.5 | 2.5 | – | – | 2.18 ± 0.20 | 2.74 ± 0.30 |
| | 5 | 7.5 | 4.20 ± 0.20 | 6.80 ± 0.25 | 84%[b] | 90.7%[b] |
| Seawater | 0 | 0 | 7.50 ± 0.40 | nd | 7.36 ± 0.30 | nd |
| | 5 | 5 | – | – | 11.57 ± 1.18 | 4.28 ± 0.16 |
| | 10 | 10 | 16.50 ± 1.60 | 10.60 ± 1.35 | 90%[b] | 106%[b] |
| | 20 | 20 | 26.70 ± 0.70 | 20.10 ± 1.40 | 96%[b] | 100%[b] |

[a] Average ± one standard deviation of three trials; nd: not detected.
[b] Recoveries from spiked samples for FAAS determination.

sample are shown in Table 4. Though Ag can react with chloride ion to form AgCl precipitate in normal case, the accurate quantification of Ag ion in matrix containing high concentration of chloride ions is still feasible, because Ag–DDTC complex is more stable than AgCl.

## 4. Conclusion

It has been shown that the one-step D-CPE procedure is an efficient and selective sample preparation method for eliminating complicated sample matrices. By selecting a proper chelating reagent, other metal ions besides $Cu^{2+}$ and $Ag^{+}$ would also be simultaneously preconcentrated with this procedure; and the enriched ions may also be determined by other sensitive atomic spectrometric methods, such as ET-AAS. Compared with a dual-step D-CPE procedure, the current technique features simplicity, rapidness and low consumption of reagents. It has a promising future in the determination of trace metal ions in complicated matrix samples or trace metal impurities in high-purity materials.

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