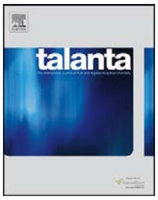
Talanta 82 (2010) 993–996

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta



# Displacement-dispersive liquid–liquid microextraction coupled with graphite furnace atomic absorption spectrometry for the selective determination of trace silver in environmental and geological samples

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ARTICLE INFO

*Article history:*
Received 28 February 2010
Received in revised form 27 May 2010
Accepted 1 June 2010
Available online 9 June 2010

*Keywords:*
Displacement-dispersive liquid–liquid microextraction
Silver
Graphite furnace atomic absorption spectrometry
Environmental and geological samples

ABSTRACT

A novel displacement-dispersive liquid–liquid microextraction method was developed for the selective determination of trace silver in complicated samples by graphite furnace atomic absorption spectrometry. This method involves two steps of dispersive liquid–liquid microextraction (DLLME). Firstly, copper ion reacted with diethyldithiocarbamate (DDTC) to form Cu-DDTC complex and extracted with DLLME procedure using carbon tetrachloride (extraction solvent) and methanol (dispersive solvent); then, the sedimented phase was dispersed into the sample solution containing silver ion with methanol and another DLLME procedure was carried out. Because the stability of Ag-DDTC is larger than that of Cu-DDTC, $Ag^+$ can displace $Cu^{2+}$ from the pre-extracted Cu-DDTC and thus the preconcentration of $Ag^+$ was achieved. Potential interference from co-existing transition metal ions with lower DDTC complex stability was largely eliminated as they cannot displace $Cu^{2+}$ from Cu-DDTC complex. The tolerance limits for the co-existing ions were increased by a long way compared with conventional DLLME. Under the optimal conditions, the limit of detection was 20 ng $L^{-1}$ ($3\sigma$) for silver with a sample volume of 5.0 mL, and an enhancement factor of 72 was achieved. The proposed method was successfully applied to determine of trace silver in some environmental and geological samples with satisfactory results.

## 1. Introduction

Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation procedures as they lead inherently to a minimum solvent and reagent consumption and drastic reduction of laboratory wastes [1]. Dispersive liquid–liquid microextraction (DLLME) is a novel liquid–liquid extraction protocol developed under this context [2]. DLLME is based on ternary component solvent systems. An appropriate mixture of an extraction solvent and a dispersive solvent, with high miscibility in both aqueous and organic phase (extraction solvent) is rapidly injected into the sample solution (aqueous phase). By this procedure a cloudy solution is produced, which is consisted of fine droplets of the extraction solvent, dispersed throughout the aqueous solution. Consequently, the analyte is extracted into the fine droplets of extraction solvent directly (generally hydrophobic organic compounds) or after complex formation (usually metal ions reaction with a suitable hydrophobic ligand). After centrifugation, the fine droplets are settled down at the bottom of the conical test tube, removed by a syringe and analyzed by chromatography or spectrometry methods. The advantages of the DLLME method are simplicity of operation, rapidity, low cost, high recovery and enrichment factors [3]. This method has been applied for determination of organic compounds [4,5] as well as for metals [6–8] and metalloids [9,10] in various types of samples but mainly in water samples.

In conventional DLLME preconcentration of metal ions, hydrophobic metal-chelate formation is the first step [11]. Obviously, many ligands have little selectivity towards metal ions. In other words, competition for the complexing agent from other co-existing transitional metal ions with target analyte cannot be avoided, and this may cause undesirable interferences. In fact, all metal-chelate based preconcentration systems have encountered such problems. Adding of a masking agent or increasing the concentration of the complexing agent is a choice, but the effectiveness may be marginal and the risk of contamination could be created. Recently, Yan et al. have successfully developed a displacement-sorption preconcentration protocol for highly selective quantification of metal ions in complicated matrices [12]. The principle of this technique is based on the stability difference of metal complexes. The targeted metal ($M_1$) with higher complex stability ($M_1$-L, L is the ligand) can take the place the other metal ($M_2$) with lower complex stability from its complex ($M_2$-L), whereas the reverse reaction cannot occur. Through the displacement reaction,

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doi:10.1016/j.talanta.2010.06.004

**Table 1**
Operating parameters for GFAAS.

| Parameters | |
|---|---|
| Lamp current/mA | 2.0 |
| Wavelength/nm | 328.1 |
| Slit/nm | 0.4 |
| Ar flow rate/mL min$^{-1}$ | 200 (stopped during atomizing) |
| Sample volume/μL | 20 |
| Temperature program | |
| Drying | 120 °C (Ramp 15 s, Hold 10 s) |
| Pyrolysis | 500 °C (Ramp 5 s, Hold 15 s) |
| Atomizing | 1900 °C (Ramp 0 s, Hold 3 s) |
| Cleaning | 2100 °C (Ramp 1 s, Hold 3 s) |

interferences from the co-existing ions due to the competition for the ligand could be greatly eliminated. This displacement-sorption preconcentration method has been successfully applied for the determination of mercury in environmental and biological samples [13,14], methylmercury in fish samples [15], palladium in road dusts [16] and silver in water samples [17]. A displacement-cloud point extraction coupled was also developed by employing the same principle, and applied for the selective determination of silver [18].

In this work, the displacement reaction principle was employed in dispersive liquid–liquid microextraction of metal ions, and a displacement-dispersive liquid–liquid microextraction (D-DLLME) method was developed for the selective determination of silver. In the proposed D-DLLME method, diethyldithiocarbamate (DDTC) was selected as the chelating agent and $Cu^{2+}$ was employed as the pre-extraction metal ion for the best selectivity of displacement. In the D-DLLME method, the DLLME procedure was carried out twice during a single sample pretreatment process: firstly, $Cu^{2+}$ was complexed with DDTC and subjected to DLLME process; secondly, after removing the aqueous phase, the sedimented phase was dispersed into the sample solution containing silver ion with methanol and another DLLME process was carried out. Because the stability of Ag-DDTC is greater than that of Cu-DDTC, $Ag^{+}$ can replace $Cu^{2+}$ from the pre-extracted Cu-DDTC complex and enter the sedimented phase. Then, the sedimented phase was subjected to graphite furnace atomic absorption spectrometer for the determination of Ag. According to the stability order of DDTC complex [19], only $Hg^{2+}$, $Pd^{2+}$ and $Ag^{+}$ can displace $Cu^{2+}$ from the complex of Cu-DDTC. Therefore, the interference arising from the competition for DDTC by transition metal ions with $Ag^{+}$ in conventional DLLME was largely eliminated, while the selective preconcentration of Ag was achieved.

## 2. Experimental

### 2.1. Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, China) with a deuterium background correction and a GF990 graphite furnace atomizer system was used. A silver hollow-cathode lamp was used as radiation source at 328.1 nm. The optimum operating parameters for GFAAS are given in Table 1. All measurements were carried out in the integrated absorbance (peak area) mode. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments CO. LTD., Shanghai, China). A Model 0412-1 centrifuge (Shanghai Surgical Instrument Factory, Shanghai, PR China) was used to accelerate the phase separation. A MK-III microwave digestion system (Shinco institute of microwave digestion technology, Shanghai, China) was used to dissolve the solid samples.

### 2.2. Standard solution and reagents

Stock standard solution (1000 μg mL$^{-1}$) of Ag was obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution. The solution of DDTC was prepared by dissolving appropriate amount of DDTC (AR, Shanghai Chemistry Reagent Company, Shanghai, China) in methanol. All other reagents used were of the highest available purity and of at least analytical reagent grade. Doubly distilled water was used throughout. Pipettes and vessels in the experiments were kept in 10% nitric acid for at least 24 h and subsequently washed four times with double distilled water.

### 2.3. Displacement-dispersive liquid–liquid microextraction procedure

Aliquots of 5.0 mL sample solution containing 10 μg mL$^{-1}$ Cu, 0.06 mg mL$^{-1}$ DDTC and 0.03 mol L$^{-1}$ $HNO_3$ was placed in a 10 mL screw cap glass test tube with conic bottom. The amount of 0.5 mL of methanol (dispersive solvent) containing 48 μL of carbon tetrachloride ($CCl_4$, extraction solvent) was injected rapidly into the sample solution by using 1.00 mL syringe. A cloudy solution (water, methanol, and $CCl_4$) was formed in the test tube, and the complex of Cu with DDTC was extracted into the fine droplets of $CCl_4$. Then, the solution was centrifuged at 3500 rpm for 5 min, and the dispersed fine droplets of $CCl_4$ were deposited at the bottom of conical test tube (about 38 μL). After removing the aqueous phase, the sedimented phase was dissolved with 0.2 mL methanol and injected into 5.0 mL sample solution containing Ag and 0.03 mol L$^{-1}$ $HNO_3$, and then another DLLME process was carried out. In this step, Ag can replace Cu from the pre-extracted Cu-DDTC complex and enter into the extraction solvent phase. After centrifuging, 20 μL of the sediment phase at the bottom of conical test tube (about 25 μL) was removed using a 50 μL microsyringe and injected into the GFAAS for the determination of Ag.

Calibration was performed against aqueous standards submitted to the same D-DLLME procedure. A blank submitted to the same procedure described above was measured parallel to the sample and calibration solutions.

### 2.4. Samples preparation

Three certified reference materials (GBW07303 stream sediments, GBW07403 soil and GBW07207 ore, obtained from Perambulation Institute of Physical Geography and Geochemistry of Geological and Mineral Ministry, Langfang, PR China) were used to check the accuracy of the developed method. The compositions of the samples could be found in the website of the supplier of the samples (www.gbw114.org). All samples were dried in an oven at 60 °C. A Portion (0.1–0.5 g) of the dried samples was accurately weighed into a PTFE vessel, treated with 6 mL of HF, 5 mL of concentrated $HNO_3$ and 3 mL of concentrated $H_2SO_4$. Then the vessel was submitted to a power program in the microwave oven. The heating steps with duration of 5 min each and a power of 250, 400 and 650 W were applied. The program was repeated twice to obtain a clear solution. The solution was heated to near dryness and the residue was dissolved in 0.1 mol L$^{-1}$ $HNO_3$. The final volume was made up to 50 mL with doubly distilled water.

## 3. Results and discussion

DLLME has been proved to be a suitable preconcentration procedure for various metal ions [11]. The optimal conditions of the extraction solvent and dispersive solvent for the DLLME preconcentration of Cu and Ag have been studied in the previous works

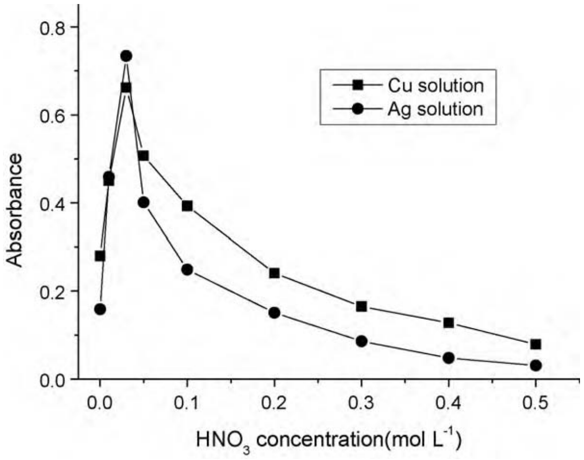

**Fig. 1.** Effect of the acid concentration of the pre-extraction solution and the sample solution on the displacement DLLME of Ag. Other experimental conditions: Cu, 10 $\mu$g mL$^{-1}$; Ag, 0.5 ng mL$^{-1}$; sample volume, 5.0 mL; dispersive solvent (methanol) volume, the pre-extraction, 0.5 mL, the displacement extraction, 0.2 mL; extraction solvent ($CCl_4$) volume, 48 $\mu$L; DDTC concentration, 0.06 mg mL$^{-1}$.

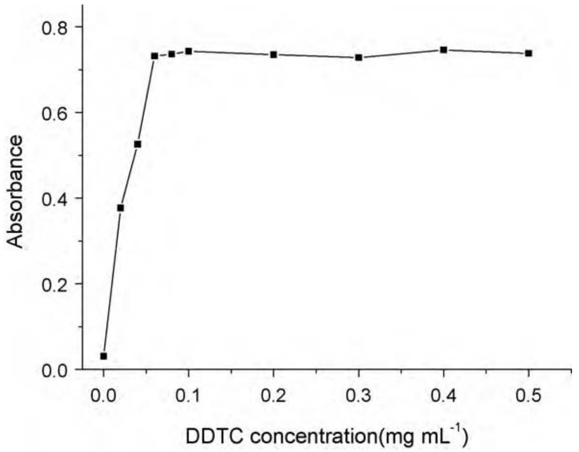

**Fig. 2.** Effect of DDTC concentration on the displacement DLLME of Ag. Other experimental conditions: Cu, 10 $\mu$g mL$^{-1}$; Ag, 0.5 ng mL$^{-1}$; sample volume, 5.0 mL; $HNO_3$ concentration in the pre-extracted solution and the sample solution, 0.03 mol L$^{-1}$; dispersive solvent (methanol) volume, the pre-extraction, 0.5 mL, the displacement extraction, 0.2 mL; extraction solvent ($CCl_4$) volume, 48 $\mu$L.

[20,21], and used directly in the first extraction process of this work. For this work, the extraction efficiency depends on the displacement reaction between Ag and Cu-DDTC. Systematic optimization of the conditions affecting the displacement reaction was therefore carried out to obtain the optimal performance of the D-DLLME procedure.

### 3.1. Pre-extraction solution acidity and sample solution acidity

The pre-extraction solution acidity (the acidity of Cu solution) influences the formation of the Cu-DDTC complex and its pre-extraction, and subsequent displacement extraction. Its effect on the absorbance signal of Ag was investigated in the range of 0–0.5 mol L$^{-1}$ $HNO_3$, and the result was shown in Fig. 1. The highest signal of Ag was obtained when $HNO_3$ concentration was 0.03 mol L$^{-1}$. Therefore, 0.03 mol L$^{-1}$ $HNO_3$ was selected for the pre-extraction process.

The sample solution acidity (the acidity of Ag solution) influences the stability of Ag-DDTC complex and the displacement reaction. The effect of sample acidity on the absorbance signal of Ag was investigated in the range of 0–0.5 mol L$^{-1}$ $HNO_3$, and the result was also present in Fig. 1. It can be seen that the highest signal of Ag was obtained at a $HNO_3$ concentration of 0.03 mol L$^{-1}$. So 0.03 mol L$^{-1}$ $HNO_3$ was used for the sample solution in the second extraction process.

### 3.2. Effect of DDTC concentration

The concentration of DDTC has a direct effect on the formation of the Cu-DDTC complex and its pre-extraction, as well as the displacement reaction between Ag and Cu-DDTC. The effect of DDTC concentration on the absorbance signal of Ag was investigated in the range of 0–0.5 mg mL$^{-1}$, and the result was shown in Fig. 2. It can be seen that the absorbance signal of Ag increased with the increase of DDTC concentration up to 0.06 mg mL$^{-1}$, and then remained constant. Thereby, a DDTC concentration of 0.06 mg mL$^{-1}$ was selected for the further study.

### 3.3. Effect of Cu concentration

The Cu concentration influences the amount of pre-extracted Cu-DDTC and subsequent the displacement reaction. Studies on the effect of Cu concentration showed that the absorbance signal of Ag increased with the increase of Cu concentration until 10 $\mu$g mL$^{-1}$ and then remained constant with further increase in Cu concentration up to 20 $\mu$g mL$^{-1}$. For further experiments, a Cu concentration of 10 $\mu$g mL$^{-1}$ was used.

### 3.4. Effect of volume of the dispersive solvent

In the second extraction process, the sedimented phase of the first extraction process was dispersed into the sample solution using methanol as the dispersive solvent. The effect of the volume of methanol on the absorbance signal of Ag was studied. It was found that the absorbance of Ag decreased remarkably after the volume of methanol exceeded 0.20 mL. In order to disperse the sedimented phase sufficiently, 0.20 mL methanol was used as the dispersive solvent in the second extraction process.

### 3.5. Effects of co-existing ions

In conventional DLLME procedure, the interference was due to the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with the analyte. Due to the introduction of displacement reaction, the selectivity of displacement sorption preconcentration and displacement-cloud point extraction was largely improved. The same effect was also expected in D-DLLME method. The effects of several potentially interfering species were carefully studied and the results were shown Table 2, and the results for the conventional DLLME method were also present [21]. Compared with the conventional DLLME method, the developed D-DLLME method gave over two orders of magnitude improvement in the tolerable limit of co-existing heavy metal ions. In the case of Pd and Hg, the low tolerable limit

**Table 2**
Tolerance limits of co-existing ions[a].

| Co-existing ions | Tolerance limits ($\mu$g mL$^{-1}$) | |
|---|---|---|
| | Displacement DLLME | Conventional DLLME |
| $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ | 5000 | 2000 |
| $Al^{3+}$ | 3000 | 100 |
| $Cd^{2+}$, $Mn^{2+}$, $Zn^{2+}$ | 1500 | 1 |
| $Co^{2+}$, $Ni^{2+}$, $Pb^{2+}$ | 1000 | 0.5 |
| $Fe^{3+}$, $Cr^{3+}$ | 500 | 0.5 |
| $Pd^{2+}$, $Hg^{2+}$ | 0.5 | 0.5 |

[a] Ag concentration, 0.5 ng mL$^{-1}$.

**Table 3**
Comparison of the published methods with the proposed method in this work.

| Enrichment method | Detection method | Enrichment factor | Detection limit ($\mu g L^{-1}$) | Reference |
|---|---|---|---|---|
| Coprecipitation | FAAS | 26 | 0.6 | [22] |
| LLE | FAAS | 30 | 13 | [23] |
| SPE | FAAS | 25 | 1.05 | [24] |
| SPE | FAAS | 110 | 0.2 | [17] |
| CPE | FAAS | 46 | 2.2 | [25] |
| CPE | ETAAS | 60 | 12 ng $L^{-1}$ | [26] |
| DLLME | FAAS | 16 | 1.2 | [27] |
| DLLME | GFAAS | 132 | 12 ng $L^{-1}$ | [21] |
| D-DLLME | GFAAS | 72 | 20 ng $L^{-1}$ | This work |

**Table 4**
Analytical results for Ag in certified reference materials ($\mu g g^{-1}$, mean ± $\sigma$, $n = 5$).

| Samples | Found | Certified value |
|---|---|---|
| GBW07303 stream sediments | 0.56 ± 0.05 | 0.58 ± 0.07 |
| GBW07403 soil | 0.095 ± 0.015 | 0.091 ± 0.011 |
| GBW07207 ore | 0.36 ± 0.02 | 0.33 ± 0.01 |

was observed due to their higher stability of DDTC complexes over Ag-DDTC. However, the content of Pd or Hg is usually not higher than Ag in many common samples. Large amounts of alkaline and alkaline earth metal ions have no interferences on the D-DLLME extraction of Ag because they cannot complex with DDTC or displace Cu from Cu-DDTC. These results clearly demonstrated the high selectivity of the developed D-DLLME method for the determination of trace Ag.

### 3.6. Detection limits and precision

For the purpose of quantitative analysis, a calibration curve for Ag with concentrations ranging over four orders was obtained and extracted under the optimal conditions. Linearity was observed over the range of 0.1–5.0 ng $mL^{-1}$ with a correlation coefficient ($R^2$) of 0.9996. The limit of detection (LOD), based on a signal-to-noise ratio (S/N) of 3, was 20 ng $L^{-1}$. The precision of this method was determined by analyzing standard solution at 0.5 ng $mL^{-1}$ of Ag for seven times in continuous, and the relative standard deviation (R.S.D.) was 2.7%. The enhancement factor, calculated as the ratio of the calibration curve slopes for Ag before and after the preconcentration step, was 72 for 5.0 mL sample solution.

Table 3 compares the characteristic data of the present method with other preconcentration methods for Ag reported in literatures. Generally, the detection limit and enhancement factor obtained by the present method are comparable to those reported methods, and the tolerable limit of co-existing ions has been greatly improved.

### 3.7. Analytical application

In order to establish the validity of the proposed procedure, the method has been applied to determine Ag in environmental and geological certified reference materials (GBW07303 stream sediments, GBW07403 soil and GBW07207 ore). The analytical results are given in Table 4. As can be seen, the determined values were in good agreement with the certified values despite the complicated matrices of these samples.

## 4. Conclusion

The results obtained in this work demonstrated that the developed D-DLLME preconcentration with GFAAS determination is a simple, rapid, selective and sensitive method for the determination of Ag in complicated samples. The proposed method effectively minimized the interference from co-existing heavy metal ions without the need of any masking reagents. The method was shown to be promising for routine application for the determination of trace amount of Ag in relatively complicated matrices.

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