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Comparison of ultrasound-assisted cloud point extraction and ultrasound-assisted dispersive liquid liquid microextraction for copper coupled with spectrophotometric determination

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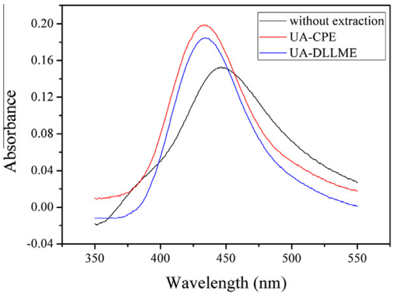
HIGHLIGHTS

- A comparative study of UA-CPE and UA-DLLME was firstly carried out.
- Sensitivity of conventional spectrophotometer was improved via the couplings.
- Be useful in less developed area without advanced analytical instruments.

GRAPHICAL ABSTRACT

A comparative study of UA-CPE and UA-DLLME was carried out. The two methods considerably improved the analytical performance of conventional spectrophotometer via the established couplings.



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ABSTRACT

In this work, ultrasound-assisted cloud point extraction (UA-CPE) and ultrasound-assisted dispersive liquid liquid microextraction (UA-DLLME) were investigated and compared firstly as ultrasound-assisted liquid phase microextraction methods, which were coupled with spectrophotometer for copper preconcentration and detection. Compared to conventional CPE and DLLME, the extraction patterns were changed and improved by the effect of ultrasound. As novel methods, their applications were expanded and the analytical performance of spectrophotometric determination for copper was considerably improved. The influence factors of UA-CPE and UA-DLLME were studied in detail. Under the optimal conditions, the limits of detection (LODs) for copper were 0.7 μg L^{-1} of UA-CPE and 0.8 μg L^{-1} of UA-DLLME with sensitivity enhancement factors (EFs) of 17 and 16. The developed methods were applied to the determination of trace copper in real water samples with satisfactory analytical results.

Introduction

As sample pre-treatment methods, solvent extraction techniques have been developed for decades to separate and pre-concentrate target analytes from bulk matrix. From traditional liquid phase extraction (LPE) to miniaturized liquid phase microextraction (LPME) [1,2], such techniques keep developing to improve analytical performance of instruments and selectivity of analytical methods. The development and application of such techniques and methods has become one of the academic hotspots in the field of analytical chemistry, including cloud point extraction (CPE) [3–5], dispersive liquid liquid microextraction (DLLME) [6,7], single drop microextraction (SDME) [1,2,8], hollow fiber-liquid phase microextraction (HF-LPME) [9–11] and etc.

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Recently, ultrasound has been introduced into LPME to develop some ultrasound-assisted extraction methods. Ultrasound is a type of energy, which can accelerate reactions, mass transfer and extraction process through accelerating the interactive rate between extractant and aqueous phase under the effect of ultrasonic wave [12,13]. Such ultrasound-assisted liquid phase microextraction methods including ultrasound-assisted cloud point extraction (UA-CPE) [12–14], ultrasound-assisted dispersive liquid liquid microextraction (UA-DLLME) [15–18], ultrasound-assisted liquid phase microextraction (UA-LPME) [19,20], ultrasound-assisted hollow fiber-liquid phase microextraction (UA-HF-LPME) [21,22] and etc. have been established and coupled with different analytical instruments for detection of organic compounds and metal elements. Among these works, analytes of interest were mainly focused on organic compounds and metal ions were seldom concerned, especially for UA-CPE.

UA-CPE was one of improved CPE methods, which used ultrasonic wave to assist CPE process to accelerate the reactions and clouding phenomena. For UA-DLLME, ultrasound was utilized to replace conventional disperser solvent of DLLME. By effect of ultrasound, the extractant could be efficiently dispersed into fine droplets to accomplish extraction of target analytes. In this work, UA-CPE and UA-DLLME were compared and coupled with conventional spectrophotometer to determine copper. Compared to some sensitive but expensive and energy consuming instruments, spectrophotometer is very cost-effective and widely used even in some less developed area. Through coupling with some advanced preconcentration techniques, its sensitivity could be improved to accomplish some trace or ultra-trace metal analysis [14,23,24].

The purpose of this work was to compare the analytical performance of the two ultrasound-assisted extraction methods. To the best of our knowledge, this was the first comparative study of the two methods. As improved extraction methods, UA-CPE and UA-DLLME have not been widely applied especially for metal analysis. This study expanded their applications and the analytical performance of conventional spectrophotometer was considerably improved through the developed couplings.

The main parameters influencing extraction and determination were investigated in detail. The analytical performance of the two methods was compared in this work. The characteristics and performance parameters were described below.

Experimental

Apparatus

UV-vis Spectrophotometer Model TU-1901 (Beijing Puxi General Instrument Co., Ltd, Beijing, China) was used for the determination.

An ultrasonic cleaner with temperature control Model SB5200DT (Ultrasonic power: 200 W, Ultrasonic frequency: 40 kHz, Ningbo Xinzhi Biotechnology Co., Ltd, Ningbo, China) was used for ultrasonic extraction for UA-CPE and UA-DLLME.

A centrifuge Model TDL-5-A (Shanghai Anting Scientific Instrument Factory, Shanghai, China) was used for phase separation experiments in 40 mL conical tubes.

The pH values were measured by a pH-meter Model pHS-25 (Shanghai Hongyi Instrument Co., Ltd, Shanghai, China).

A laboratory pure water system Model DZG-303A (Chengdu Tangshi Kangning Science and Technology Development Co., Ltd, Chengdu, China) was used to prepare ultra pure water.

Reagents

Copper standard solution (1000 mg L^{-1}) was purchased from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (Beijing, China). Working standard solution was obtained daily by stepwise dilution from standard stock solution in ultra pure water. Non-ionic surfactant Triton X-114 (TX-114) (Sigma-Aldrich) was used as extractant for UA-CPE. Tetrachloromethane (CCl_4, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was used as extractant for UA-DLLME. Diethyldithiocarbamate (DDTC, The Sixth Factory of Chemical Reagent, Tianjin, China) was used as the chelating reagent for copper. Other chemical reagents were all of analytical grade.

Ultra pure water was used throughout to decrease blank.

Procedures of UA-CPE and UA-DLLME

The procedure of UA-CPE was similar with traditional CPE and relatively time-consuming. For each sample, 40 mL analytical solution containing copper and proper concentration of DDTC was mixed in a centrifugal tube. After adjusting the pH value, the optimal concentration of TX-114 was added into the conical tube. Ultrasound was applied to assist and accelerate cloud point extraction under the equilibration temperature of 55 °C for 20 min in an ultrasonic cleaner with temperature control.

UA-DLLME was also accomplished in a 40 mL centrifugal tube. For each sample, 40 mL analytical solution containing copper and proper concentration of DDTC was mixed in the tube. After adjusting the pH value, the extractant (CCl_4) was injected rapidly into the tube by a syringe. After that, the extraction was accomplished under the effect of ultrasound in an ultrasonic cleaner for 10 min. The solution became turbid and CCl_4 was dispersed into fine droplets to capture the target analytes.

After centrifugation at 3000 rpm for 5 min, the turbid solution became clear and the enriched phase presented deeply color. The water phase was removed carefully and then ethanol was used to dilute the concentrated sample to 3 mL for determination, considering the sampling demand of spectrophotometer.

Sample collection and preparation

Real water samples were all collected from local place. Lake water was collected from Erhai Lake (Dali, China). River water was collected from Xier River (Dali, China). Tap water was collected from our lab. Bottled mineral water and cola drink were purchased from a local market. All the environmental water samples were filtered through a 0.45 μm micropore membrane prior to use. The resultant samples were then subjected to the established UA-CPE and UA-DLLME and subsequently analyzed by spectrophotometer.

Results and discussion

Study on the absorption spectra of complex

In this work, spectrophotometric determination was coupled with UA-CPE and UA-DLLME. The maximum wavelength of absorption for the resultant samples was the basis of the quantification analysis. In the preliminary experiments, the resultant samples were conveyed to the spectrophotometer to measure the absorption curves, according to the experimental procedures described above. For direct detection of copper, the complex of Cu-DDTC was determined in the range of wavelength from 350 nm to 550 nm. During the experiment, the concentration of 1000 μg L^{-1} copper was used for wavelength scan without preconcentration. For UA-CPE and UA-DLLME, 100 μg L^{-1} of copper was used to be pre-concentrated and detected (without optimization for both methods). From the results in Fig. 1, for both methods the preliminary enhancement of sensitivity was obvious and the extraction