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Determination of trace bismuth by using a portable spectrometer after ultrasound-assisted dispersive liquid–liquid microextraction

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In this work, ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME) was first coupled with a portable tungsten coil electrothermal atomic absorption spectrometer (W-coil ET-AAS) for trace bismuth detection. A conventional disperser solvent in DLLME was substituted by the ultrasound effect, which could afford more effective emulsification and make the extraction method greener. This technique was effectively coupled with a portable W-coil ET-AAS instrument to improve the analytical performance and expand the application of this spectrometer. Under the optimal conditions, the limit of detection (LOD) for bismuth was 0.2 μg L^{-1}, with a sensitivity enhancement factor (EF) of 72. After routine optimization experiments accomplished in the lab, the developed coupling was applied to the field analysis of environmental samples with satisfactory analytical results.

1. Introduction

Dispersive liquid–liquid microextraction (DLLME) has been widely applied in analytical chemistry since established by Assadi *et al.* in 2006.[1] This technique has been widely coupled with different instrumental methods for metal detection in recent years, including flame atomic absorption spectrometry (FAAS),[2,3] graphite furnace atomic absorption spectrometry (GF-AAS),[4,5] inductively coupled plasma optical emission spectrometry (ICP-OES),[6] inductively coupled plasma mass spectrometry (ICP-MS),[7] *etc.* Based on conventional DLLME, some advanced studies have been developed to improve its extraction efficiency and expand its applications, such as ultrasound-assisted DLLME (UA-DLLME),[8–10] surfactant assisted-DLLME (SA-DLLME),[11,12] temperature-controlled IL-DLLME,[13] cold-induced aggregation DLLME,[14] solvent terminated DLLME (ST-DLLME),[15] and solvent-based de-emulsification-DLLME (SD-DLLME).[16]

Ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME) has been developed recently to improve conventional DLLME. The effect of conventional disperser solvents such as methanol, ethanol, acetonitrile or acetone in DLLME was substituted by ultrasound-assisted emulsification. Compared to conventional DLLME, the effect of emulsification and the efficiency of extraction were considerably improved in the UA-DLLME method.[10,17] UA-DLLME has not been widely applied and most of its applications were coupled with some advanced analytical instruments for the detection of organic compounds.[18–20] In this work, the newly developed technique was first coupled with a portable tungsten coil electrothermal atomic absorption spectrometer (W-coil ET-AAS) for trace bismuth determination. Through this coupling, the applications for both UA-DLLME and W-coil ET-AAS were expanded.

The portable tungsten coil electrothermal atomic absorption spectrometer is a newly developed electrothermal atomic absorption spectrometer based on a tungsten coil atomizer, a charge coupled device (CCD)[21,22] and years of academic accumulation in the field of W-coil ET-AAS.[23–27] This instrument is designed as a portable spectrometer, which can be applied in field analysis and move traditional AAS analysis out of the lab. The sensitivities for some metal ions such as cadmium, chromium, and manganese are relatively good enough to accomplish direct detection for some environmental samples. For many other metals, the sensitivities cannot afford directly accurate determination in real samples. In order to improve its analytical performance and expand its applications, some preconcentration methods are necessary to be coupled with this portable spectrometer.[28]

To the best of our knowledge, the UA-DLLME technique was first coupled with a portable W-coil ET-AAS instrument for trace bismuth determination in this work. Bismuth is slightly toxic and similar to lead *in vivo* metabolism, which can cause chronic poisoning. Bismuth entering the body distributes mainly in the kidney and then in the liver. Analyzing and monitoring the content of bismuth in environmental samples is significant. Through this established coupling, the sensitivity of the portable spectrometer for bismuth was considerably improved. In this work, the coupling was successfully applied in field analysis of trace bismuth in some environmental water samples.

The main parameters influencing extraction and determination were investigated in the lab in detail. The characteristics

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and analytical performance of the established coupling were described below.

2. Experimental

2.1. Apparatus

A portable tungsten coil electrothermal atomic absorption spectrometer model WFX-910 (Beijing Rayleigh Analytical Instrument Co., Ltd., Beijing, China) was investigated as a new commercial instrument. Overall dimensions (length × width × height): 610 mm × 230 mm × 335 mm and weight: 18 kg. As shown in Fig. 1 for the schematic diagram of the instrument principle, the instrument consisted of three main parts arranged horizontally, including a hollow cathode lamp (HCL), a W-coil atomizer enclosed in a quartz cell and a spectrometer-charge coupled device (CCD). Argon containing 20% H_2 is used to prevent the coil from oxidizing and to produce a reducing environment during atomization. The instrument is equipped with a customized box to be carried out conveniently. A rechargeable lithium battery is equipped with the portable instrument to provide enough power for field analysis without commercial power supply. A specially customized and portable cylinder of argon containing 20% H_2 is equipped with this spectrometer for field analysis. The heating programs for bismuth are summarized in Table 1.

A centrifuge Model 80-2 (Jiangsu Jintan Yitong Electronic Co., Ltd., Jiangsu, China) was used for phase separation.

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

An Ultrasonic cleaner Model SB25-12D (ultrasonic power: 600 W, ultrasonic frequency: 40 kHz, Ningbo Xinzhi Bio-technology Company Co., Ltd., Ningbo, China) was used to accomplish the ultrasound extraction process.

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.

2.2. Reagents

Bismuth standard solution (1000 mg L^{-1}) was purchased from National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (Beijing, China). The working standard solution was obtained daily by stepwise dilution from the standard stock solution in ultra pure water. Tetrachloromethane (CCl_4, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as the extractant. Dithizone (The Sixth Factory of Chemical Reagent, Tianjin, China) was used as the chelating reagent. Other chemical reagents were all of analytical grade.

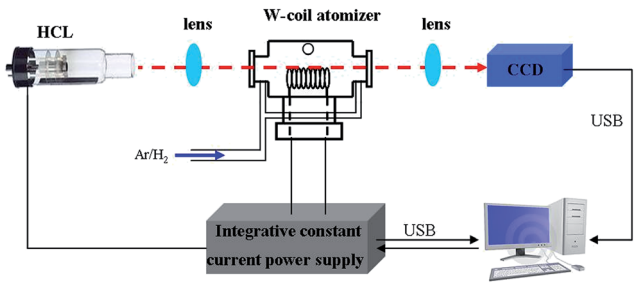

Fig. 1 Schematic diagram of the principle for a portable W-coil ET-AAS instrument.

2.3. Ultrasound-assisted dispersive liquid–liquid microextraction procedure

In this work, the preconcentration procedure was accomplished in a 10 mL calibrated conical tube. The optimum concentration of the chelating agent dithizone was added into the metal solution. After adjusting the pH value, the extractant (CCl_4) was rapidly injected into the tube by using a syringe. The extraction was then assisted and accomplished under the effect of ultrasound in an ultrasonic cleaner for 4 min. The solution became turbid and CCl_4 was dispersed into fine droplets to capture the formed hydrophobic complexes. After centrifugation, the turbid solution became clear and the organic rich phase was settled at the bottom of the tube. Then 10 μL of the resultant organic rich phase was directly drawn into a pipette and injected onto the W-coil atomizer for detection. This was very simple and rapid without any excessive dilution and removal of the water phase before determination.

2.4. Sample collection and preparation

Several real water samples were collected to validate the application of the established method, especially in field analysis. Bottled mineral water was purchased in a local market. Tap water was collected in our laboratory after flowing for about 5 min. River water was collected from Xier River (Dali, China) and lake water was collected from Erhai Lake (Dali, China). Waste water was collected in a local factory. All the real water samples above were filtered through a 0.45 μm micropore membrane prior to use. The environmental samples were field-analyzed by using the portable spectrometer after UA-DLLME in order to validate the application in field analysis of this developed coupling.

3. Results and discussion

3.1. Optimization of instrumental parameters

For a portable W-coil ET-AAS spectrometer, routine optimization should be carried out for the detection of the target element, including the desolvation current, pyrolysis current, atomization current, duration for each step and carrier gas flow rate of Ar/H_2. As listed in Table 1, the optimum W-coil heating procedures (including the applied current and duration for each step) were found for the determination of bismuth in the resultant organic rich phase after SA-DLLME. The current and duration for desolvation and pyrolysis were very crucial for successful detection, which should remove the matrix of the organic solvent thoroughly and not lose bismuth due to excessive heating. The W-coil surface temperature in the atomization step was about 2400 °C, which guaranteed the atomization efficiency. Considering the individual differences of tungsten

Table 1 Heating program of the potable spectrometer (sampling amount: 10 μL)

Step		Desolvation	Pyrolysis	Cooling	Atomization	Cleaning
With UA-DLLME	Current (A)	2.8	2.8	0	9.0	9.0
	Duration (s)	15	10	4	4	2
Without UA-DLLME	Current (A)	2.8	2.8	0	9.0	9.0
	Duration (s)	30	10	4	4	2

coils as well as the production of circuit boards and other factors, the heating procedure is not immutable and frozen. Specific optimization of the current and lasting time should be carried out when changing tungsten coils or using different instruments. After optimization, the optimal carrier gas flow rate of Ar/H_2 (mL min^{-1}) was 800/200. The position of the hollow cathode lamp (HCL) and the charge coupled device (CCD) was recommended by the instrument manufacturer. The peak-height absorbance at 223.0 nm was used for quantification. The sampling amount used in this developed method was 10 μL of the organic rich phase.

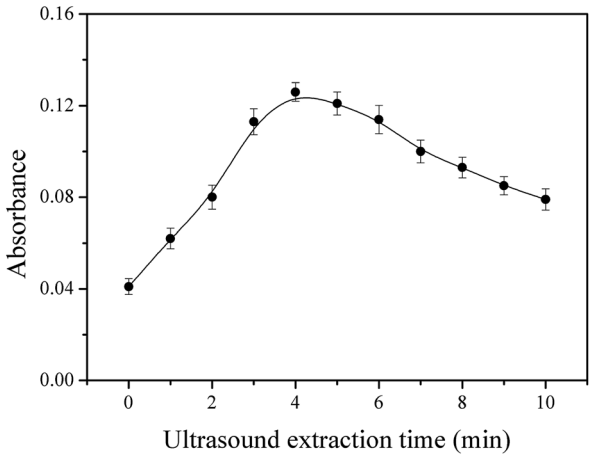

Fig. 2 Optimization of the ultrasound extraction time. UA-DLLME conditions: Bi, 5.0 μg L^{-1}; dithizone, 5.0×10^{-5} mol L^{-1}; CCl_4, 200 μL; pH, 3.0; sample volume, 10 mL. The error bars stand for "± one standard deviation of three trials".

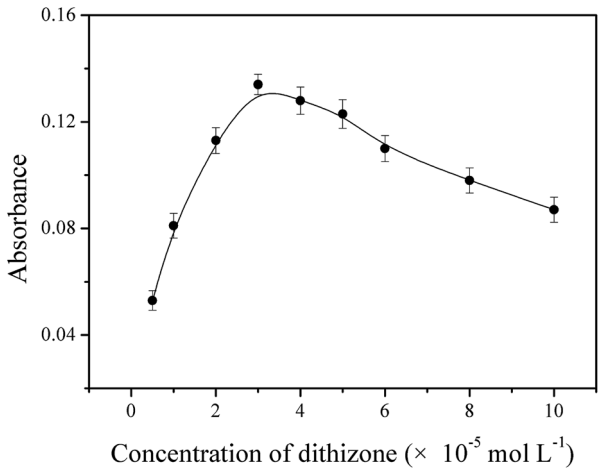

Fig. 3 Optimization of the dithizone concentration. UA-DLLME conditions: Bi, 5.0 μg L^{-1}; CCl_4, 200 μL; pH, 3.0; sample volume, 10 mL; ultrasound extraction time, 4 min. The error bars stand for "± one standard deviation of three trials".

3.2. Investigation of UA-DLLME parameters

The main parameters influencing extraction were investigated, including the effect of the ultrasound extraction time, chelating reagent, extractant, pH and conditions of phase separation. The ionic strength had no significant influence on the extraction efficiency of DLLME based on our previous work,[29] which was not optimized in this work.

3.2.1. Effect of the ultrasound extraction time. In this work, the ultrasound extraction time was important in emulsification and mass transfer. The factor remarkably affected the extraction efficiency of the established method. In this work, the ultrasound extraction time was investigated in the range from 0 to 10 min. As shown in Fig. 2, it was found that the absorbance of bismuth increased with the ultrasound extraction time increasing from 0 to 4 min. When the extraction time was longer than 4 min, the absorbance decreased obviously. The longer ultrasound extraction time could lead to the temperature increase of the solution, and the complexation of bismuth and dithizone would be affected thus decreasing the extraction efficiency of UA-DLLME. Excessive ultrasound may cause the dissolution of the extractant thus decreasing the mass transfer efficiency. After optimization, the optimal condition of the ultrasound extraction time in this system was found to be 4 min.

3.2.2. Concentration of the chelating reagent. As the principle reagent, dithizone could be well complexed with many metal ions including bismuth,[30] which was selected to form the Bi–dithizone complex in this work. The standard stock solution of dithizone (1.0×10^{-3} mol L^{-1}) was daily prepared by dissolving an appropriate amount of dithizone in tetrahydrofuran. The effect of dithizone concentrations on the absorbance was investigated in the range of 0.5×10^{-5} to 1.0×10^{-4} mol L^{-1}, as shown in Fig. 3. It was found that the absorbance increased with the increase of dithizone concentrations in the range of 0.5×10^{-5} to 3.0×10^{-5} mol L^{-1} and at higher dithizone concentrations, the absorbance obviously decreased. The excessive chelating agents could be co-extracted into the organic phase, thus decreasing the extraction efficiency of target analytes. Therefore, 3.0×10^{-5} mol L^{-1} of dithizone was chosen as the optimal condition of UA-DLLME for further experiments.

3.2.3. Optimization of the extractant. For the established method, careful attention should be paid to the type of extractant and its volume, which could obviously affect the extraction efficiency of the improved method. In this section, some conventional extractants such as dichloromethane, chloroform, tetrachloromethane and octanol were investigated. The results indicated that higher signals of the absorbance were obtained when CCl_4 was selected. CCl_4 could form a stable cloudy solution and has less consumption of volume. After the selection of the extractant type, the optimization of the volume of CCl_4 was carried out in the range of 100–500 μL and the results are shown in Fig. 4. The results demonstrated that the signals increased dramatically when the volume of the extractant increased from 100 μL to 150 μL. A continuous increase of the volume of CCl_4 led to the decrease of signals. Although the phase ratio of the aqueous phase and organic phase was higher when a smaller volume of extractant was selected, the mass transfer efficiency was the first key factor in the extraction system. In this work, the volume of CCl_4 below 150 μL could not afford high efficiency of mass transfer. When the volume was higher than 150 μL, the signal decreased by the effect of phase ratio decrease. As a result, 150 μL was the reasonable volume for the experiment.

3.2.4. Effect of the pH. In the extraction of metal ions, the extraction efficiencies are closely related to the pH of the solution system. The proper acidity of solution is the key factor for the formation of the complex. Thus, in order to obtain the desired preconcentration efficiencies, the pH values were studied in the ranges of 2.0–10.0 adjusted by diluted HCl and $NH_3 \cdot H_2O$. The results shown in Fig. 5 indicated that the complex of Bi–dithizone required a certain amount of acidity. When the pH of solution increased from 2.0 to 5.0, the absorbance signals increased correspondingly. The stronger alkalescence obviously induced the decrease of absorbance signals. Hereby, a pH of 5.0 was selected in the further experiments.

3.2.5. Conditions of phase separation. Centrifugation was carried out to assist and accelerate phase separation after UA-DLLME. After this treatment, the turbid solution became clear and the organic phase with concentrated target analytes was settled to the bottom of the tube. The experimental conditions were investigated to find out the optimal centrifugation rate and time. It was found that the optimal condition of phase separation was 3500 rpm for 3 min. Then 10 μL of the resultant organic rich phase was directly drawn into a pipette and injected onto the W-coil atomizer for detection. This was very simple and rapid without removal of the water phase before determination.

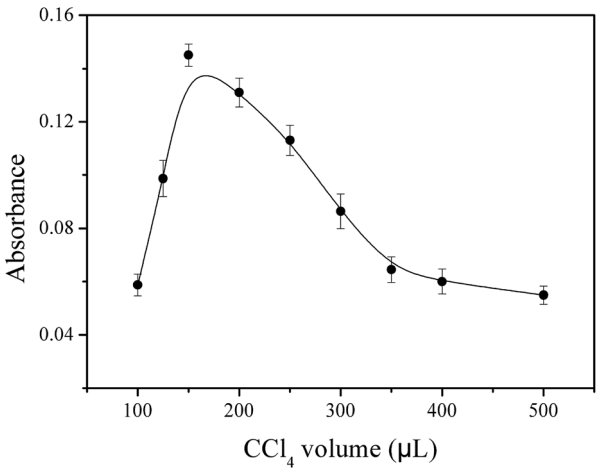

Fig. 4 Optimization of the volume of the extractant. UA-DLLME conditions: Bi, 5.0 μg L^{-1}; dithizone, 3.0 × 10^{-5} mol L^{-1}; pH, 3.0; sample volume, 10 mL; ultrasound extraction time, 4 min. The error bars stand for "± one standard deviation of three trials".

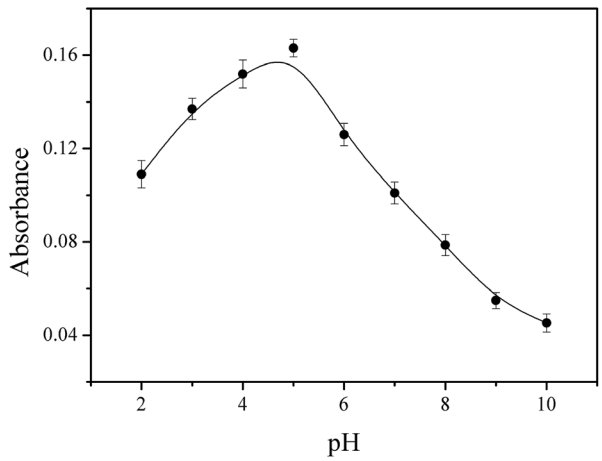

Fig. 5 Effect of the pH. UA-DLLME conditions: Bi, 5.0 μg L^{-1}; dithizone, 3.0 × 10^{-5} mol L^{-1}; CCl_4, 150 μL; sample volume, 10 mL; ultrasound extraction time, 4 min. The error bars stand for "± one standard deviation of three trials".

3.3. Interference

Because dithizone could complex with other metal ions besides bismuth, interference may occur due to the competition of other heavy metal ions for the chelating agent. The subsequent co-extraction of other formed complex with Bi–dithizone could

Table 2 Tolerant limits of coexisting ions for the determination of Bi (5.0 μg L^{-1})

Potential interfering ions	Interference/Bi (w/w)	Recovery (%)
K^+	30 000	93.1
Na^+	50 000	107
Ca^{2+}	3000	92.8
Mg^{2+}	4000	96.3
Cl^-	50 000	106
Cu^{2+}	100	93.3
Al^{3+}	200	97.8
Fe^{3+}	100	105
Mn^{2+}	200	94.5
Pb^{2+}	50	92.7
Cd^{2+}	200	93.8
Sb^{3+}	20	91.2
Zn^{2+}	100	106
Co^{2+}	100	94.6
Ni^{2+}	50	92.3

Table 3 Analytical characteristics

	With UA-DLLME	Without UA-DLLME
Calibration equation (μg L^{-1})	$A = 0.0288C + 0.0073$	$A = 0.0004C - 0.0045$
Linear dynamic range, LDR (μg L^{-1})	2–30	250–2500
LOD[a] (μg L^{-1})	0.2	17
Absolute LOD[b] (pg)	2	170
R^2 (correlation coefficient)	0.9943	0.9981
RSD ($n = 7$, after UA-DLLME)	4.7% (5.0 μg L^{-1})	
Sensitivity enhancement factor[c]	72	

[a] LOD, limit of detection, was based on the 3σ criterion for 11 blank measurements. [b] Absolute LOD, with quality as the unit to represent the detection limit, the LOD was multiplied by the sampling volume. [c] Sensitivity enhancement factor was calculated by the slope ratio of the calibration curves for Bi determination with and without UA-DLLME.

also decrease the extraction efficiency. To evaluate the selectivity of the developed coupling system, the effect of typically potential interfering ions was investigated and the results are shown in Table 2 (the tolerable limit was taken as a relative error ≤10%). According to the data, some major matrix ions in natural water samples have no obvious interference, while some other heavy metal ions have less tolerable limits due to the competition and co-extraction effect.

3.4. Analytical figures of merit

Analytical figures of merit for the established UA-DLLME-W-coil ET-AAS coupling were obtained under optimal conditions and are summarized in Table 3. At least 0.9943 of R^2 (correlation coefficient) showed good linearity of the calibration curves. It can be seen from Table 3 that superior sensitivity of bismuth detection was obtained after UA-DLLME preconcentration. The UA-DLLME method showed high extraction efficiency, simplicity and rapidity, which could be well coupled with this portable spectrometer in lab or field analysis.

3.5. Determination of bismuth in real water samples

Considering the biological and environmental significance, several real and certified water samples were analyzed to validate the accuracy and applicability of the developed method. After the routine optimization experiments accomplished in the lab, the environmental samples were field-pre-concentrated and analyzed by using the portable W-coil ET-AAS spectrometer. Bottled mineral water and tap water were analyzed in the lab.

Table 4 Analytical results for bismuth in real water samples (Avg. ± SD of three trials)

Real sample	Found in the natural sample (μg L^{-1})	Spiked (μg L^{-1})	Recovery (%)
Tap water	ND[a]	5.0	95.8
Erhai Lake	3.5 ± 0.2	5.0	104
Xier River	4.3 ± 0.2	5.0	96.7
Mineral water	ND[a]	5.0	103
Waster water	13.2 ± 0.7	10	95.1

[a] ND, not detected.

The analytical results are summarized in Table 4. The recoveries for the spiked samples were in the acceptable range of 95.1–104%.

4. Conclusions

In this work, the ultrasound-assisted dispersive liquid–liquid microextraction (UA-DLLME) method was first coupled with W-coil ET-AAS. Compared to DLLME, the effect of emulsification and the efficiency of extraction could be considerably improved when ultrasound was used to substitute conventional disperser solvents. Through the coupling, the limit of detection for bismuth was 0.2 μg L^{-1}, with a sensitivity enhancement factor (EF) of 72. The analytical performance of this portable spectrometer for bismuth was considerably improved. The developed method was applied to the field analysis of some environmental samples with satisfactory analytical results.

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