Cloud Point Extraction of Cr, Cu, Cd, and Pb From Water Samples and Determination by Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry with Isotope Dilution

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INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for trace multielement and isotopic analysis and has been satisfactorily applied to the analysis of diverse samples. However, high saline solutions can cause both spectral and non-spectral interferences. Spectral overlaps are seen from polyatomic ions derived from matrix elements such as Na, Ca, Cl, and S. Changes in analyte count rates are observed with high levels of salt or heavy matrix ions. To alleviate these interferences and also to determine elements such as Cr, Cu, Cd, and Pb, whose concentrations are at sub ng/mL levels, matrix separation is an alternative. Among various matrix separation and pre-concentration procedures, ion exchange and solid phase extraction using chemically modified sorbents with complexing agents are the most popular (1-3).

Recently, several reports have been published on the analytical use of non-ionic surfactants in the cloud point extraction (CPE) of trace elements applied especially to water samples (4-7). Due to their simplicity, high recoveries, high pre-concentration factors, and limited solvent consumption, these methods have gained growing acceptance (8,9). When the CPE technique was used for the extrac-

ABSTRACT

A simple and efficient cloud point extraction procedure is described for the simultaneous pre-concentration and separation of trace levels of Cr, Cu, Cd, and Pb from water samples and their determination by electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). The method was based on the formation of hydrophobic complexes of Cr, Cu, Cd, and Pb with ammonium pyrrolidine dithiocarbamate (APDC), followed by their extraction into a small volume of surfactant-rich phase using a non-ionic surfactant, Triton X-114. The main parameters affecting the extraction process, such as concentration of the complexing agent and pH and the amount of Triton X-114, were optimized. The surfactant-rich phase was dissolved with nitric acid in ethanol and then injected into the ETV-ICP-MS for Cr, Cu, Cd, and Pb determination. The pre-concentration factor was 14. Isotope dilution was used for quantification. The limits of detection for Cr, Cu, Cd, and Pb were 4, 2, 1, and 1 pg mL⁻¹, respectively. The accuracy of the procedure was verified by analyzing certified reference materials NRCC SLRS-4 River Water and NRCC SLEW-3 Estuarine Water. The reported procedure was applied for the analysis of different types of real world water samples such as tap water, reservoir water, and Love River water collected in the city.

tion of metal chelates, the atomic spectrometric techniques, such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), were often used as detectors (10). The combination of CPE with electrothermal vaporization sample introduction achieved much higher sensitivity compared to CPE in combination with conventional pneumatic nebulization (9,11).

In the present work, we describe a simple microwave-assisted cloud point extraction procedure for the simultaneous separation and pre-concentration of Cr, Cu, Cd, and Pb at ultra trace levels in water samples and determination by electrothermal vaporization (ETV) ICP-MS with isotope dilution (ID). A non-ionic surfactant, Triton® X-114 (12,13), and ammonium pyrrolidine dithiocarbamate (APDC) (14-16) were used as the extracting and complexing agent, respectively. The hydrophobic APDC-metal complexes formed were extracted into a small volume of the surfactant-rich phase (SRP) generated on heating the solution. In recent years, microwave-assisted extraction has been used effectively for cloud point extraction of metal chelates from various matrices (13,17-20). The major advantage of the procedure is efficient extraction of species, even at lower temperatures, and acceleration of

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extraction. Isotope dilution (ID) methods have been used in several previous ICP-MS applications to ensure accurate determinations (21,22). Since another isotope of the same element represents the ideal internal standard for that element, ID results are expected to be highly accurate even when the sample contains high concentrations of concomitant elements and/or losses occur during sample preparation or during sample introduction into the ICP. The main factors affecting the extraction efficiencies and the effect of ETV conditions on ion signals were evaluated meticulously. The procedure is applied for the determination of Cr, Cu, Cd, and Pb in NRCC SLRS-4 River Water and SLEW-3 Estuarine Water and also real water samples collected locally.

EXPERIMENTAL

Instrumentation

An ELAN® 6100 DRC™ II ICP-MS (Perkin-Elmer, Inc., Shelton, CT, USA) was used for the determination of Cr, Cu, Cd and Pb. The instrumental operating conditions are listed in Table I.

The samples were introduced using an HGA®-600MS electrothermal vaporizer (PerkinElmer, Inc., Shelton, CT, USA). The instrumental operating conditions are listed in Table II. Pyrolytically coated graphite tubes with platforms of the same material were used throughout. The transfer line consisted of a 90-cm long, 6-mm i.d. PTFE tubing. The sample introduction system included a Model AS-60 autosampler equipped with a USS-100 ultrasonic slurry sampler (PerkinElmer, Inc., Shelton, CT, USA). Polystyrene autosampler cups were used. The slurry sampler was set at 25 W (40% power) with a 5-second mixing time for the slurries before injection of 10-μL sample aliquots for analysis.

A CEM MARS (Matthews, NC, USA) microwave digester, equipped with a temperature sensor, was used for the extraction of Cr, Cu, Cd and Pb from water samples (13). The dissolved surfactant-rich phase was introduced into the plasma by a cross-flow pneumatic nebulizer with a Scott-type spray chamber.

Reagents and Standard Solutions

All solutions were prepared with ultrapure water (18.2 MΩ cm) obtained from a Millipore® Milli-Q™ water purification system (Bedford, MA, USA). The solutions of APDC

(Sigma-Aldrich, Buchs, Switzerland) and non-ionic surfactant Triton® X-114 (Sigma, Steinheim, Germany) were prepared in water without further purification. Ethanol and nitric acid (Suprapur®, Merck, Darmstadt, Germany) were used for dissolving the surfactant-rich phase. A multielemental working standard at 1 ng mL⁻¹ was prepared daily by dilution of the 10 μg mL⁻¹ stock SPEX-2 solution (Spex, Metuchen, NJ, USA) with diluted HNO₃. Enriched isotopes of ⁶⁵CuO (99.7%) and ¹¹¹CdO (96.4%) were purchased from the Oak Ridge National Laboratory (Oak Ridge,

TABLE I
ICP-MS Instrumental Operating Conditions

ICP-MS instrument	ELAN® 6100 DRC™ II
RF Power	1350 W
Plasma argon flow rate	15 L min ⁻¹
Auxiliary argon flow rate	1.13 L min ⁻¹
Carrier argon flow rate	0.98 L min ⁻¹
Dwell time	10 ms
Scan mode	Peak hopping
Sweeps/Reading	2
Reading/Replicate	130
Signal measurement	Integrated
Isotope monitored	⁵² Cr, ⁵³ Cr, ⁶³ Cu, ⁶⁵ Cu, ¹¹¹ Cd, ¹¹³ Cd, ²⁰⁶ Pb, ²⁰⁸ Pb
DRC Parameters	
Cell gas	NH ₃
Flow rate	0.6 mL min ⁻¹
Rpa	0
Rpq	Cr (0.65), Cu (0.8), Cd (0.5), Pb (0.7)
Axial field potential	225 V

TABLE II
HGA-600MS Temperature Programming

Step	Temperature (°C)	Ramp Time (s)	Hold Time (s)	Gas Flow Rate (mL min ⁻¹)	Read
Dry	150	10	10	300	-
Pyrolysis	250	15	5	300	-
Vaporization	2200	0	8	0	ON
Cooling	20	5	2	300	-
Condition	2600	1	5	300	-
Cooling	20	5	10	300	-

TN, USA), and $^{53}\text{Cr}_2\text{O}_3$ (96.9%) was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). $^{206}\text{Pb}(\text{NO}_3)_2$ was obtained from Merck, Darmstadt, Germany. The interference studies were performed by using varying amounts of single-element stock standard solutions of Ca (AccuTrace, New Haven, CT, USA), Mg (Riedel-de Haen, Seelze, Germany), and Na and K prepared from NaCl and KCl (Merck, Darmstadt, Germany). Humic acid was obtained from Aldrich, USA. All containers were soaked in 20% (v/v) nitric acid for 24 hours and cleaned with Milli-Q water before use.

Cloud Point Extraction Procedure

To study the effect of CPE conditions on extraction, a 10-mL solution containing 1 ng mL⁻¹ each of Cr(III), Cu, Cd, and Pb was taken into a pre-cleaned centrifuge tube and 0.01–0.75 mL of 10% (m/v) APDC and 0.05–0.9 mL of 10% (m/v) Triton® X-114 were added. To these solutions, various pH buffer solutions were added and the solutions mixed well for two minutes.

In this study, a simple and rapid microwave-assisted extraction procedure was used for the extraction of Cr, Cu, Cd, and Pb from water samples. The centrifuge tubes were put into a 1000-mL beaker. The microwave system was programmed to maintain the water temperature in the range 30–70 °C for 5–40 minutes which led to phase separation. Separation of the aqueous and surfactant-rich phases was accomplished by centrifugation for 10 minutes at a relative centrifugal force of 3743 g (MIKRO 22R, Hettich, Germany), where $g = (1.118 \times 10^{-5}) R S^2$ (R =radius of rotor in centimeters and S =speed of centrifuge in rpm). The surfactant-rich phase, formed at the bottom of the container, was easily separated by decanting the bulk aqueous phase after cooling

the solution in an ice bath for 10 minutes. For pneumatic nebulization ICP-MS, after addition of 1 ng mL⁻¹ Rh as the internal standard, the surfactant-rich phase was dissolved to 10 mL with 1% (v/v) HNO₃. Procedural blanks were also prepared in a similar manner.

Sample Preparation

The applicability of the method was initially verified with certified reference materials NRCC SLRS-4 River Water and NRCC SLEW-3 Estuarine Water (National Research Council of Canada, Ottawa, Canada) and applied to real world samples such as Love River water, tap water, and reservoir water samples obtained locally. For the cloud point extraction, aliquots of 10 mL of sample solution, 0.5 mL 10% (m/v) APDC and 0.5 mL 10% (m/v) Triton® X-114 were added into a 15-mL centrifuge tube. After addition of a suitable amount of enriched isotopes, the mixture was buffered to pH 5.0 with acetic acetate. The Cr, Cu, Cd, and Pb enriched isotopes spiked were 0.110, 0.320, 0.009, and 0.012 ng mL⁻¹ in Love River water; 0.13, 0.15, 0.002, and 0.020 ng mL⁻¹ in tap water; 0.094, 0.47, 0.4, 0.003 and 0.110 ng mL⁻¹ in reservoir water; 0.26, 0.63, 0.002 and 0.023 ng mL⁻¹ in SLRS-4; 0.065, 0.54, 0.009, and 0.002 ng mL⁻¹ in SLEW-3. The microwave system was programmed to maintain the water temperature at 60 °C for 15 minutes. Separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 10 minutes at 3743 g. For the determination of Cr, Cu, Cd, and Pb in water samples, the surfactant-rich phase was dissolved with 0.2 mL of 0.5% HNO₃ in ethanol; then 10 µL of the resultant solution was directly introduced into the graphite tube for the determination of Cr, Cu, Cd, and Pb by ETV isotope dilution ICP-MS. Procedural blanks were prepared in a similar manner.

Since there are no reference values for the real world samples and in order to check the accuracy of the ETV-isotope dilution-ICP-MS method, we compared the analyte concentrations in the samples using the present procedure to those obtained by other methods. Due to the difference in the transport efficiency and the non-spectral interferences between the aqueous solution and dissolved surfactant-rich phase, the slopes obtained by external calibration were different from the matrix-matched calibration method. To achieve accurate results, the matrix-matched calibration method was selected in the following analysis.

For matrix-matched calibration, various concentrations of Cr, Cu, Cd, and Pb standard solutions were extracted; the surfactant-rich phases obtained were dissolved and injected into ETV-ICP-MS for Cr, Cu, Cd, and Pb determination. The signals obtained were used to make the calibration curves.

RESULTS AND DISCUSSION

Optimization of Cloud Point Extraction Parameters

The CPE efficiency depends on the hydrophobicity of the ligand and the complex formed, the apparent equilibrium constants in the micelle medium, the kinetics of the complex formation, and the transfer between the phases. The pH plays an important role on metal chelate formation and subsequent extraction. The pKa of APDC is 3.29. The effect of pH on the recoveries of Cr, Cu, Cd, and Pb in the surfactant-rich phase was evaluated at pH values varying between 4 and 6.5. As can be seen from Figure 1, the recovery of Cr increased with an increase in pH when the pH was less than 5.0. The recoveries of Cu and Pb did not change significantly in the pH range of 4.0–6.0. Based on these results, pH 5.0 was used for the extraction of

Cr, Cu, Cd, and Pb from water samples.

The variation of the analytical signal as a function of the concentration of APDC in the range of 0.01–0.75% (m/v) was studied, and the experimental results are shown in Figure 2. It can be seen that the analytical signal for Cr increased rapidly as the concentration of APDC increased from 0.01% (m/v) to 0.5% (m/v), and remained constant with a concentration of APDC up to 0.75% (m/v). The concentration of APDC did not significantly affect the recoveries of Cu, Cd, and Pb between 0.05–0.75% (m/v). For further studies, an APDC concentration of 0.5% (m/v) was selected.

Compared to Triton X-100, Triton X-114 has a lower cloud point temperature (18 °C) and a higher density of the surfactant-rich phase which makes it more conducive for inducing the phase separation and collecting the surfactant-rich phase by centrifugation. Hence, Triton X-114 was selected for CPE. The effect of Triton X-114 concentration upon sensitivity and extraction was studied within the surfactant concentration range of 0.05–0.9% (m/v). Figure 3 shows the effect of

Triton X-114 concentration on the signal intensity of Cr, Cu, Cd, and Pb in the surfactant-rich phase. As shown, the recoveries did not change significantly when the concentration of Triton X-114 was larger than 0.5% (m/v). To achieve a larger enhancement factor, a minimum amount of Triton X-114 needs to be used. Therefore, a Triton X-114 concentration of 0.5% (m/v) was employed for further studies.

The effect of incubation temperature on the recoveries was investigated by microwave heating from 30 °C to 70 °C, which produced good phase separation in this range. It was found that the recoveries did not change with an increase in incubation temperature. An incubation temperature of 60 °C was chosen. Keeping the incubation temperature of 60 °C, the influence of incubation time on CPE was studied within the range of 5–40 minutes. As shown in Figure 4, the recoveries of Cr and Cu increased with an increase in the incubation time when the incubation time was less than 15 minutes. Hence, a 15-minute incubation time was adopted throughout the experiments.

Since both Cr(III) and Cr(VI) might be present in real water samples and to check the difference of the extraction efficiency of Cr(III) and Cr(VI), solutions of 2 ng mL⁻¹ of Cr(III), 2 ng mL⁻¹ of Cr(VI), and a mixture of 1 ng mL⁻¹ Cr(III) and 1 ng mL⁻¹ Cr(VI) was extracted independently with the selected CPE procedure. This experiment showed that the recoveries of Cr(III), Cr(VI), and the mixture of Cr(III) and Cr(VI) were 100, 100, and 97%, respectively. Cr(VI) could also be extracted efficiently. This could be due to the fact that Cr(VI) was reduced to Cr(III) by APDC and formed the Cr-APDC complex, which was efficiently extracted into the surfactant-rich phase (23).

When a sample solution containing large concentrations of Ti and Mo is analyzed by ICP-MS, there could be polyatomic interferences on the determination of Cu and Cd due to the formation of TiO⁺ and MoO⁺. The recoveries of Ti and Mo under the selected CPE conditions were also studied. From the experiments it was found that the recoveries of Ti and Mo were 63% and 80%, respectively. The use of ETV sample introduction has been proved to alleviate the oxide inter-

Fig. 1. Dependence of the recoveries on pH of sample solution. The concentration of APDC and Triton X-114 was 0.5% (m/v) and 0.3% (m/v), respectively. Microwave-assisted extraction was set at 40 °C for 20 minutes.

Fig. 2. Recovery dependence on APDC concentration. The pH value of the solution was adjusted to 5.0.

ference effectively (24,25). Since the recoveries of Ti and Mo are significant, to minimize the TiO and MoO interferences and to achieve a better enhancement factor, ETV sample introduction was selected for the analysis of real samples. For cloud point extraction, ETV sample introduction is preferred over solution nebulization due the fact that the volume of the surfactant-rich phase is much lower (few μL) and can therefore be injected into the ETV system with little dilution. In addition, for solution nebulization, the surfactant-rich phase requires higher dilution which then reduces the enhancement factor.

Interferences of Coexisting Ions

The effect of potential interferences of some metal ions on the pre-concentration and determination of Cr, Cu, Cd, and Pb was examined. In these experiments, solutions containing 1.0 ng mL^{-1} of Cr, Cu, Cd, and Pb added with interfering ions (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) were treated according to the recommended procedure under the optimum conditions. From the experiment it was found that the recoveries were in the range of 90–110% when the ratio of analyte to interferent was as large as $1:10^5$. Moreover, when the 1 ng mL^{-1}

standard solution was spiked with $5 \mu\text{g mL}^{-1}$ humic acid, another compound normally present in water samples, the recoveries of Cr, Cu, Cd, and Pb were in the range of 90–94%. These experiments demonstrate that the recoveries of Cr, Cu, Cd, and Pb from water using cloud point extraction will not be significantly affected by matrix components.

Selection of Pyrolysis and Vaporization Temperatures

After extraction, the surfactant-rich phase was dissolved with 0.2 mL of 0.5% HNO_3 in ethanol, and then 10 μL of the resultant solution was directly introduced into the graphite tube for the determination of Cr, Cu, Cd, and Pb by ETV-ICP-MS. Figure 5 shows the effect of pyrolysis temperature on the ion signals when the vaporization temperature was set at 2000°C . As shown, the ion signals of Cd and Pb increased with an increase in pyrolysis temperature, whereas the ion signal of Cr increased up to 250°C , and then decreased gradually. However, the signal of Cu decreased slightly when the pyrolysis temperature was increased. The decrease in the ion signals of Cr and Cu at

Fig. 3. Effect of incubation time on recoveries. $\text{pH} = 5.0$, $(\text{APDC}) = 0.5\%$ (m/v), $(\text{TX-114}) = 0.5\%$ (m/v). Incubation temperature was set at 60°C .

Fig. 4. Effect of pyrolysis temperature on the ion signals. Injected solution contained the extract of 1 ng mL^{-1} Cr, Cu, Cd, and Pb standard solution. Vaporization temperature was set at 2000°C . All data were relative to the first point.

Fig. 5. Effect of pyrolysis temperature on the ion signals. Injected solution contained the extract of 1 ng mL^{-1} Cr, Cu, Cd, and Pb standard solution. Vaporization temperature was set at 2000°C . All data were relative to the first point.

higher temperatures is possibly due to the decomposition of their APDC complexes. For the simultaneous determination of the elements studied, the pyrolysis temperature was set at 250 °C in the following experiments. Figure 6 shows the effect of vaporization temperature on the ion signals when the pyrolysis temperature was set at 250 °C. From these experiments we found that the Cr and Cu ion signals increased with an increase in vaporization temperature when the temperature was less than 2200 °C. The vaporization temperature did not affect the signals of Cd and Pb significantly. In the following experiments, 2200 °C was selected as the vaporization temperature.

Selection of DRC Conditions

The determinations of Cr, Cu, and Cd by ICP-MS are known to suffer from various polyatomic ion interferences. For instance, $^{52}\text{Cr}^+$ and $^{53}\text{Cr}^+$ are interfered by $^{40}\text{Ar}^{12}\text{C}^+$ and $^{40}\text{Ar}^{12}\text{CH}^+$, and $^{40}\text{Ar}^{13}\text{C}^+$, respectively, and $^{63}\text{Cu}^+$ and $^{65}\text{Cu}^+$ are interfered by $^{47}\text{Ti}^{16}\text{O}^+$, $^{40}\text{Ar}^{23}\text{Na}^+$ (less in ETV-ICP-MS), and $^{49}\text{Ti}^{16}\text{O}^+$, respectively, and the cadmium isotopes are interfered by various molybdenum oxide ions. Since the ETV sample introduction technique was employed in this work, the oxide and hydroxide ion interferences could be alleviated to an insignificant level (26). The measured ratios of TiO^+/Ti^+ and MoO^+/Mo^+ were reduced from

0.3% and 0.6% to 0.05% and 0.02%, respectively, when ETV sample introduction was employed. Hence, interferences were not found on the measurements of Cu and Cd. Though there is a possibility of interference of $^{40}\text{Ar}^{23}\text{Na}^+$ on $^{63}\text{Cu}^+$, in the present study it was not found to be significant in accordance with earlier reports (24,27). In contrast, from the experiments we found large backgrounds at m/z 52 ($^{40}\text{Ar}^{12}\text{C}^+$) and 53 ($^{40}\text{Ar}^{12}\text{CH}^+$ and $^{40}\text{Ar}^{13}\text{C}^+$) at the optimized conditions when the ICP-MS instrument was operated under the standard mode. The ArC^+ and ArCH^+ background ions could be reduced to an insignificant level when the DRC™ mode was employed while NH_3 was used as the reaction gas (28,29). Thus, NH_3 was selected as the DRC reaction gas in this study. The usual parameters, namely cell gas flow rate, value of rejection parameter q (RP q) and the axial field voltage (AFV) were optimized in this study.

Spectral Interferences Study

For ICP-MS analysis, the components of the sample could produce several polyatomic ions which interfere in the determination of various elements. The determination of Cr, Cu, and Cd was interfered by various background ions. In order to evaluate the significance of these interferences, the following experiments were performed to check the interferences caused by Ti and Mo in the water samples. A 1 ng mL⁻¹ amount of Cu and Cd standard solution was spiked with 500 ng mL⁻¹ Ti and 1000 ng mL⁻¹ Mo. These solutions were injected for the determination of $^{63}\text{Cu}/^{65}\text{Cu}$ and $^{111}\text{Cd}/^{113}\text{Cd}$ isotope ratios using ETV-ICP-MS. The isotope ratio was calculated from the peak areas of each injection peak. The spiked concentrations were much higher than the concentration of matrix elements present in the water samples analyzed.

Fig. 6. Effect of vaporization temperature on the ion signals. Pyrolysis temperature was set at 250 °C. All data were relative to the first point.

From these experiments we found that the isotope ratios of $^{63}\text{Cu}/^{65}\text{Cu}$ and $^{111}\text{Cd}/^{113}\text{Cd}$ were not affected by Ti and Mo at these concentrations in accordance with the Student's *t*-test for a confidence level of 95%. The alleviation of the interferences was due to the introduction of a much drier aerosol with the ETV sample introduction device. These experiments demonstrate that the concentrations of Cu and Cd in the water samples can be determined by ETV-ICP-MS without significant interferences.

Validation of the Method and Analysis of Real Samples

The method developed was employed for the determination of Cr, Cu, Cd, and Pb in various water samples. Isotope dilution quantification was employed to minimize the non-spectral interference caused during the extraction process and ETV-ICP-MS determination. The accuracy of the proposed cloud point extraction procedure was verified by analyzing certified reference materials NRCC SLRS-4 River Water and NRCC SLEW-3 Estuarine Water. Typical ETV-ICP-MS signals of Cr, Cu, Cd, and Pb for

the extract of SLEW-3 are shown in Figure 7 and the analysis results are listed in Table III. The determined concentrations in the River Water and Estuarine Water reference samples were in good agreement with the certified values at the 95% confidence interval. In case of real samples, for which no reference values are available, there was also good agreement between the values of the isotope dilution method and the matrix-matched calibration method. The results of this study indicate that Cr, Cu, Cd, and Pb in water samples can be readily quantified by the proposed CPE-ETV-ID-ICP-MS method.

The detection limit was estimated from the matrix-matched calibration curves as the signal equal to three standard deviations of the reagent blank. The limits of detection of Cr, Cu, Cd, and Pb were 4, 2, 1, and 1 pg mL^{-1} , respectively. The detection limits can be improved if pure chemicals are used for extraction. A comparison of the limits of detection and enhancement factors obtained by this method and the reported methods is given in Table IV. As can be seen, the limits of detection

obtained in the reported procedure are superior to those reported, indicating the quantification of Cr, Cu, Cd, Pb in water samples even at lower concentrations due to the pre-concentration by using CPE and ETV-ICP-MS analysis.

CONCLUSION

The described procedure is simple and provided a pre-concentration factor of 14 for the separation of ultratrace levels of Cr, Cu, Cd, and Pb from water samples. Recoveries were in the range 90–94% and interference-free measurements ensured accurate determinations. Isotope dilution was used for quantification. The limits of detection for Cr, Cu, Cd, and Pb were 4, 2, 1, and 1 pg mL^{-1} , respectively. The procedure reported can be considered a better alternative for existing procedures since it is more eco-friendly by using a non-toxic surfactant and agreement with green chemistry principles.

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Fig. 7. ETV-ICP-MS signals of Cr, Cu, Cd, and Pb of the extract of SLEW-3.

TABLE III
Determination of Cr, Cu, Cd ,and Pb by CPE-ETV-ICP-MS^a (n = 3)

Sample	Method ^b	Cr	Concentration (µg L ⁻¹)		Pb
			Cu	Cd	
NRCC SLRS-4	Method 1	0.331 ± 0.024	1.83 ± 0.12	0.012 ± 0.003	0.087 ± 0.005
River Water	Method 2	0.329 ± 0.011	1.79 ± 0.09	0.014 ± 0.002	0.088 ± 0.003
	Certified	0.33 ± 0.02	1.81 ± 0.08	0.012 ± 0.002	0.086 ± 0.007
NRCC SLEW-3	Method 1	0.186 ± 0.018	1.65 ± 0.09	0.050 ± 0.006	0.0100 ± 0.0012
Estuarine Water	Method 2	0.188 ± 0.028	1.63 ± 0.07	0.051 ± 0.007	0.0099 ± 0.0011
	Certified	0.183 ± 0.019	1.55 ± 0.12	0.048 ± 0.004	0.009 ± 0.0014
Tap Water	Method 1	0.169 ± 0.013	0.46 ± 0.02	0.013 ± 0.006	0.095 ± 0.010
	Method 2	0.161 ± 0.012	0.43 ± 0.09	0.013 ± 0.004	0.074 ± 0.014
Reservoir Water	Method 1	0.113 ± 0.014	1.39 ± 0.01	0.019 ± 0.002	0.403 ± 0.005
	Method 2	0.119 ± 0.011	1.36 ± 0.05	0.014 ± 0.004	0.391 ± 0.011
Love River Water	Method 1	0.263 ± 0.014	1.60 ± 0.04	0.049 ± 0.007	0.113 ± 0.010
	Method 2	0.266 ± 0.013	1.64 ± 0.09	0.053 ± 0.011	0.114 ± 0.009

^a Results are means of three measurements ± standard deviation.

^b Method 1: Isotope dilution method. Method 2: Matrix-matched calibration method. Certified: NRCC certified value.

TABLE IV
**Comparison of Limits of Detection and Enhancement Factors
by the Proposed Method and the Reported Methods**

Analytical Method	Sample Preparation	LOD (ng L ⁻¹)				Enrichment Factor	Ref.
		Cd	Cu	Cr	Pb		
ETV-ICP-MS	Cloud point extraction	1	2	4	1	14	This work
ETV-ICP-OES	Cloud point extraction			220			30
ETV-ICP-OES	Cloud point extraction	100	400	200		71 (Cd), 96 (Cu), 81 (Cr)	31
ETV-ICP-MS	Single-drop microextraction	4.6			2.9	140 (Cd), 190 (Pb)	32
ETV-ICP-MS	Magnetic solid phase microextraction	0.72			1.12	>40	33
ICP-MS	Cloud point extraction	60	100		50		34
ICP-DRC-MS	Cloud point extraction			25		10	35

REFERENCES

1. B.A. Lesniewska, B.G. Zytkiewicz, A. Ruszczynska, E. Bulska, and A. Hulanicki, *Anal. Chim. Acta* 564, 236 (2006).
2. E. Rudolph, A. Limbeck, and S. Hann, *J. Anal. At. Spectrom.* 21, 1287 (2006).
3. A. Limbeck, J. Rendl, and H. Puxbaum, *J. Anal. At. Spectrom.* 18, 161 (2003).
4. E.K. Paleologos, C.D. Stalikas, S.M.T. Karayanni, G.A. Pilidis, and M.I. Karayannis, *J. Anal. At. Spectrom.* 15, 287 (2000).
5. Y. Li, B. Hu, and Z. Jiang, *Anal. Chim. Acta* 576, 207 (2006).
6. X. Zhu, X. Zhu, and B. Wang, *J. Anal. At. Spectrom.* 21, 69 (2006).
7. Y. Li, and B. Hu, *Spectrochim. Acta, Part B*, 62, 1157 (2007).
8. C.D. Stalikas, *Trends Anal. Chem.* 21, 343 (2002).
9. X. Jiang, S. Wen, and G. Xiang, *J. Hazard. Mater.* 175, 146 (2010).
10. C.B. Ojeda, and F.S. Rojas, *Anal. Bioanal. Chem.* 394, 759 (2009).
11. Y.J. Li, B. Hu, M. He, and G.Q. Xiang, *Water Res.* 42, 1195 (2008).
12. N.N. Meeravali, and S.J. Jiang, *J. Anal. At. Spectrom.* 23, 555 (2008).
13. N.N. Meeravali, and S.J. Jiang, *J. Anal. At. Spectrom.* 23, 1365 (2008).
14. E.K. Paleologos, C. D. Stalikas, S.M. Tzouwara-Karayanni, G.A. Pilidis, and M.I. Karayannis, *J. Anal. At. Spectrom.* 15, 287 (2000).
15. B.T. Jones, G.L. Donati, K.E. Pharr, C.P. Calloway, and J.A. Nobrega, *Talanta* 76, 1252 (2008).
16. J. Nan, Y. Jiang, and X.P. Yan, *J. Anal. At. Spectrom.* 18, 946 (2003).
17. M. Niemela, S.M. Huttunen, S.S. Gornostayev, and P. Peramaki, *Microchim. Acta* 166, 255 (2009).
18. A. Akinlua, M.A. Jochmann, J. Laaks, A. Ewert, and T.C. Schmidt, *Anal. Chim. Acta* 691, 48 (2011).
19. K. Simitchiev, V. Stefanova, V. Kmetov, G. Andreev, N. Kovachev, and A. Canals, *J. Anal. At. Spectrom.* 23, 717 (2008).
20. C. Sun, Y.C. Xie, Q.L. Tian, and H.Z. Liu, *Phytochem. Anal.* 19, 160 (2008).
21. Y.T. Chang, and S.J. Jiang, *J. Anal. At. Spectrom.* 23, 140 (2008).
22. K.-H. Lee, S.-J. Jiang, and H.-W. Liu, *J. Anal. At. Spectrom.* 13, 1227 (1998).
23. C.M. Andriele, N. Jakubowski, and J.A.C. Broekaert, *Spectrochim. Acta, Part B*, 52, 189 (1997).
24. M.J. Liaw, and S.J. Jiang, *J. Anal. At. Spectrom.* 11, 555 (1996).
25. H.C. Liao, and S.J. Jiang, *J. Anal. At. Spectrom.* 14, 1583 (1999).
26. Y.-J. Tseng, Y.D. Tsai, and S.J. Jiang, *Anal. Bioanal. Chem.* 387, 2849 (2007).
27. Y. C. Li, and S. J. Jiang, *Anal. Chim. Acta* 359, 205 (1998).
28. K. Neubauer, and U. Völlkopf, *At. Spectrosc.* 20, 64 (1999).
29. S.D. Tanner, V.I. Baranov, and U. Völlkopf, *J. Anal. At. Spectrom.* 15, 1261 (2000).
30. Y.J. Li, B. Hu, Z.C. Jiang, Y. and W. Wu, *Anal. Lett.* 39, 809 (2006).
31. Y. Yamini, M. Faraji, S. Shariati, R. Hassani, and M. Ghambarian, *Anal. Chim. Acta* 612, 144 (2008).
32. L. Li, B. Hu, L.B. Xia, and Z.C. Jiang, *Talanta* 70, 468 (2006).
33. B. Chen, S. Heng, H. Peng, B. Hu, X. Yu, Z. Zhang, D. Pang, X. Yue, and Y. Zhu, *J. Anal. At. Spectrom.* 25, 1931 (2010).
34. M. Fernanda Giné, A. F. Patreze, E.L. Silva, J.E.S. Sarkis, and M.H. Kakazu, *J. Braz. Chem. Soc.* 19, 471 (2008).
35. N.N. Meeravali, and S.J. Jiang, *Talanta* 80, 173 (2009).