Evaluation of Mercury Concentrations in Groundwater Samples of Coal Field Using a Matrix-less Cloud Point Extraction Procedure Prior to Analysis by Cold Vapor Atomic Absorption Spectrometry

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ABSTRACT

A novel matrix-less cloud point extraction (ML-CPE) procedure was developed for the determination of mercury (Hg) in groundwater samples collected from the Thar coalfield, Pakistan. For preconcentration of Hg, a complexing reagent, diethyl-dithiophosphate (DEDTP) was selected. Various parameters such as temperature, time, pH, and amount of complexing reagent and concentration of surfactant concentrations were studied in order to find the best conditions for the enrichment of mercury in water samples. In the proposed method, the Hg-DEDTP was subsequently entrapped in the nonionic surfactant, Triton X-114. Then, Hg was back-extracted into the matrix-less aqueous phase and determined by cold vapor atomic absorption

spectrometry (CVAAS). At optimized experimental parameters, the limit of detection and the enhancement factor were found to be 7.5 ng/L and 22.8 ng/L, respectively. The relative standard deviation (RSD) for six replicates at 5 µg/L of Hg was 4.6%, which indicates that the developed method is highly precise and repeatable. The accuracy of the method was verified by spiking the known concentration of the standards in a real sample. No significant difference ($p > 0.05$) was observed between the experimental results and the added analyte. The developed ML-CPE method was successfully applied for the preconcentration and determination of Hg in groundwater samples. The levels of Hg in the groundwater samples of the Thar coal field was in the range of 1.8–3.23 µg/L.

14). The high exposure of Hg in organic form caused the Minamata disease, a neurological syndrome, which was first observed in Minamata City, Japan, and continued to be monitored from 1932 to 1968. In 1956, Japan reported that 1043 persons had died and 2252 persons were suffering from this disease due to the elevated Hg levels in fish (15).

A coal mine can be operated in various ways such as open pit, underground methods, surface stripping, and hydraulic leaching (16). Mining generates a large amount of waste (17) which can enter into the groundwater from mine discharge, runoff, chemical weathering of rocks and soils and wet and dry fallout from atmospheric particulate matter (18). One of the routes in which Hg enters into the human body is drinking water (19). Hence, control of Hg is becoming increasingly important, especially in water sources (20). According to WHO and the European Union Guidelines for Drinking water, the permissible limit of Hg in water is 1.0 µg/L, with a mean value of 2.46 µg/L Hg (21–23).

Due to the toxicological impact of Hg concentrations in the environment, it has encouraged the development of very sensitive methodologies for its determination by techniques such as cold vapor atomic absorption spectrometry (CVAAS). However, the presence of mercury in groundwater is mostly at very low concentrations and its determination requires enrichment

INTRODUCTION

The Pakistan coal mining sector has many environmental challenges such as degradation of groundwater quality, emission of nitrogen oxide, sulfur oxide, and particulate matter from various mining activities (1, 2). In the mining sector, acid mine drainage and metals leaching into groundwater can deteriorate the water quality,

which creates health risks to aquatic and human life (3,4). Water pollution caused by mercury (Hg) contributes to biodiversity loss, environmental degradation, and human health hazards (5–8). Mercury is a non-degradable toxic metal which can accumulate in the human body causing damage to the nervous system and internal organs (9–10). High Hg concentrations cause toxicity and environmental risk (11) and enter into the environment due to the combustion of coal for power generation, waste burning, and other energy sources (12–

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steps. Among the different preconcentration methods, cloud point extraction is an interesting alternative because it produces high enrichment efficiencies and concentration factors, and uses low-cost, non-toxic reagents (24-29).

CPE is based on the hydrophobic interaction between the organo-metallic complex and the surfactant, whereas the other hydrophobic species can be extracted into the surfactant-rich phase and may interfere in the analysis of the elements of interest. The drawbacks of traditional CPE are overcome by a modified matrix-less cloud point extraction. In the proposed ML-CPE methodology of the present study, the resulting Hg complex was entrapped in a non-ionic surfactant and back-extracted in aqueous solution to minimize the adverse effects of the surfactant.

Thar Coal Field

The Thar coalfield is located in the Thar Desert, situated at the south-eastern parts of Sindh province, Pakistan, and is the largest lignite coal reserve in the world (30). It is the hottest area in the country with temperatures ranging from 28 °C to 48 °C in the summer and varies from 9 °C to 24 °C in the winter. Limited rainfall in the Thar province varies from 200 to 250 mm per year. The population of the Tharparkar province of Sindh has limited access to fresh drinking water and rely on stored rainwater and groundwater.

EXPERIMENTAL

Instrumentation

A double-beam model AAnalyst™ 700 atomic absorption spectrophotometer, coupled with an MHS-15 chemical vapor generation system, was used (PerkinElmer, Inc., Shelton, CT, USA). A single-element hollow cathode Hg lamp operated at 5 mA was used as the energy source.

The Hg signal was isolated at 253.7 nm with a spectral bandwidth of 0.7 nm. WinLab™ 32 software (PerkinElmer, Inc.) was used to process and calculate the analytical data. The centrifuge used was a model ROWKA Laboratoryjna, type WE-1, No. 6933 (Mechanika Phe-cyzyjna, Poland). The incubation time and temperature were measured by a programmable SC-121TH ultrasonic water bath (Sonicor, Deer Park, NY, USA), with a temperature range from 0 °C to 80 °C and a frequency of 35 kHz. The composite samples of groundwater were mixed with a mechanical shaker (220/60 Hz, Gallenkamp, Germany). The pH of the groundwater was maintained according to the experimental requirements using a model Ecoscan Ion 6 pH meter (Kuala Lumpur, Malaysia). The programmable microwave oven (Osaka, Japan) was used to preconcentrate the water samples. The instrumental and operating conditions are listed in Table I.

Reagents, Solutions, and Glassware

Ultrapure water obtained from a Milli-Q® water system (ELGA Laboratory, Bucks, UK) was used throughout the experimental work. A working standard solution was prepared for calibration from Hg stock standard solution (1000 mg/kg, Fluka Kamica, Buchs, Switzerland). The surfactant Triton® X-114 (tert-octylphenoxy-poly(ethoxyethanol) (Sigma-Aldrich, St. Louis, MO, USA), the complexing reagent DEDTP (Aldrich, Milwaukee, WI, USA), and NaBH₄ as the reducing agent (Aldrich, Milwaukee, WI, USA) were used. The high quality grade antifoaming agent of KMnO₄ (Sigma) was used for Hg determination (see Table I). All glassware and polyethylene bottles were thoroughly washed with water, then soaked overnight in 5.0 mol/L HNO₃ and finally thoroughly rinsed with Milli-Q® water (Millipore Corporation, USA) to remove the remaining residual acid content on the inside walls of the glassware.

TABLE I
Instrumental and Operating Parameters for
Hg Determination by CV-AAS

Instrumentation	AAnalyst™ 700 AAS
Lamp current	5.0 mA
Analytical wavelength	253.7 nm
Slit-width and height	0.7 nm, Low
Radiation source	HCL
QTA heating	No flame required
Characteristic mass	4.68 ng
Characteristic concentration	0.468 µg/L
Argon carrier gas (99.99%)	200 mL/min
Background correction	D ₂ Lamp -
Diluent/Carrier solution	1.5% HNO ₃ (v/v)
Reducing agent	3% NaBH ₄ in 1% NaOH (w/v)
Stabilizing/antifoaming agent	5% KMnO ₄ (w/v)
Pre-reaction purge time	30 s
Reaction time	5.0 s
Post-reaction purge time	40 s
Sample volume	10.0 mL

Collection of Samples

Groundwater samples from the Thar coal field were collected using the standard method (31-32) and with legal permission and assistance provided by the Sindh coal authority. The high power compressor was operated for withdrawing groundwater for drinking. All other activities of mining at the time of sampling in 2014 were continued. Twenty samples were collected and stored in washed polyethylene bottles and brought to the laboratory on same day to avoid contamination. The samples were filtered with Whatman 0.45 μm filter paper by using a vacuum pump and kept at 4°C until determination of Hg (33, 34).

ML-CPE Procedure

The ML-CPE procedure consists of two steps. First, 10.0 mL groundwater samples and standard solutions containing 0.5–10 $\mu\text{g/L}$ Hg were added into glass tubes with a stopper (20-mL capacity). Then 0.5 mL of DEDTP (0.1–0.5%) and 2.0 mL of Triton X-114 surfactant (0.1–1.0 %) were added. The pH was maintained in the range of 1.0–4.0 by adding 0.10 mol/L of

HNO_3/NaOH in acetate buffer. The resulting solution was kept at 45 °C for 10 minutes. Separation of the two phases was achieved by centrifugation at 4000 rpm for 10 minutes. The content of the tubes was placed into a container of ice to enhance the viscosity of the surfactant-enriched phase with the targeted Hg analyte, and then the remaining aqueous solution was discarded.

For the second step, the surfactant-rich phase containing the Hg complex was treated with 2.0 mL of 0.5–2.0 mol/L NaOH to leach out the Hg metal into the alkaline aqueous solution. Then the solutions were placed into a thermostatic bath at 45 °C for 10 minutes and centrifuged to separate the two phases. After ML-CPE, the supernatant was introduced into the CVAAS for the determination of Hg. The same procedure was applied for the preparation of the blanks.

RESULTS AND DISCUSSION

Optimization of ML-CPE Method

Effect of pH

The pH plays an important role on the extraction efficiency of the

ML-CPE method and also affects the overall formation of the complex between the target analyte and the complexing reagent. The effect of pH on the extraction efficiency of Hg was studied in the range of 1.0–4.0, while the other parameters were kept at their optimum levels. The complexing reagent DEDTP is selective for the formation of the complex with Hg at pH 1.5, while at pH > 2.5 the extraction efficiency of Hg decreased as is shown in Figure 1. Therefore, a pH of 1.5 was selected as optimal for the proposed method.

Effect of DEDTP Concentration

DEDTP was selected as the optimal complexing agent due to the highly hydrophobic nature of the complexes with metals/metalloid. The extraction efficiency of Hg from the groundwater samples with a DEDTP concentration ranging from 0.1–0.5% (w/v) was used. Maximum recovery of Hg was observed up to a DEDTP concentration of 0.30% (w/v), while a further increase had no effect on the recovery as is shown in Figure 2. Thus, 0.30% DEDTP concentration was selected for the effective quantification of Hg in groundwater samples.

Fig. 1. Effect of pH on pre-concentration of Hg by ML-CPE method using 2.0 $\mu\text{g/L}$ Hg; DEDTP, 0.30% (w/v); Triton X-114, 0.25% (v/v); equilibration temperature 45 °C; and time 14 minutes.

Fig. 2. Effect of DEDTP concentration on pre-concentration of Hg by ML-CPE method using 2.0 $\mu\text{g/L}$ Hg; pH 1.5; Triton X-114, 0.25% (v/v); equilibration temperature 45 °C, and time 14 minutes.

Effect of Triton X-114 Concentration

Triton X-114 is the best option in ML-CPE, because it is a non-ionic surfactant with a low cloud point temperature and enables phase-partitioning of hydrophilic solutions from amphiphilic solutions. The effect of surfactant concentration on the pre-concentration of Hg was investigated and optimized in the range of 0.1–0.45%. The effect of Triton X-114 concentration on the %recovery of Hg is shown in Figure 3. Optimum concentration of Triton X-114 was found to be 0.25% for optimum recovery of Hg. Therefore, 0.25% of Triton X-114 concentration was selected for the subsequent extraction of Hg in the ML-CPE procedures.

Effect of Temperature and Incubation Time

The extraction efficiency of Hg could be achieved when the ML-CPE process is carried out at the equilibration temperature above the cloud point temperature of the surfactant (Triton X-114). In the current work, the equilibrium temperature was studied in the range of 20–75 °C by using the ultrasonic water bath. It was observed that 45 °C was adequate for the Hg

complex. Time also plays an important role for the extraction of Hg from groundwater and therefore, the study of equilibrium time was performed in the range of 4–25 minutes. An equilibration time of 14 minutes was chosen for the quantitative extraction of Hg. The best and effective incubation temperature and time in the second step of the ML-CPE procedure was found to be 45 °C and 14 minutes, respectively.

Effect of Back-extraction of Reagents

In the second step of the ML-CPE procedure, the effect of back-extraction with the basic reagents was studied. For this purpose, 0.5–2.0 mol/L NaOH/HCl was used to back-extract Hg into the aqueous phase from the hydrophobic complexes trapped in the micelle solution (Triton X-114). Maximum Hg recovery was obtained with 1.0 mol/L of NaOH, while a 10–20% lower recovery of Hg was obtained with 1.0 mol/L HCl. Therefore, 1.0 mol/L of NaOH solution was used to back-extract Hg into the aqueous solution.

Effect of Interfering Ions

The advantages of the proposed ML-CPE method were investigated.

A series of solutions of 15.0 mL containing 50 µg/L of Hg and different concentrations of interfering ions (ClO_4^- , PO_4^{3-} , CH_3COO^- , NO_3^- , SO_4^{2-} , K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Al^{3+} , and Fe^{3+}) were subjected to the ML-CPE procedure at optimized values of the parameters. It was found that for ClO_4^- , PO_4^{3-} , CH_3COO^- , NO_3^- , SO_4^{2-} , K^+ , and Na^+ , the metal to interference ratio was 1:3500, and for Mg^{2+} , Ca^{2+} , and Ba^{2+} it was 1:1200, while for Zn^{2+} , Al^{3+} , and Fe^{3+} the ratio was 1:600. It was observed that matrix components such as alkali and alkaline earth metals have much less effect on the selectivity of the proposed method. This might be due to the fact that these metals do not form stable complexes with DEDTP. Thus, it can be stated that the proposed method can be selectively used as a separation tool for Hg determination at given tolerance limits of the coexisting ions.

Analytical Capability of ML-CPE

A linear calibration graph was achieved by using working standard solutions of Hg in the range of 0.5–10 µg/L. The analytical sensitivity was obtained by least squares regression analysis of the calibration graphs based on peak area measurements. The equation used for the calibration graph was:

$$Y = 0.1003 \text{ Hg} + 0.0068$$

where Y is the integrated value of the peak area. The limit of detection (LOD) was defined as $\text{LOD} = 3 \times \text{SD}/m$, where SD is the standard deviation corresponding to 10 blank injections and m is the slope of the calibration graph. The LOD was found to be 7.5 ng/L and is listed in Table II. The enrichment factor (EF) was estimated from the ratio of the slope of the calibration curves with and without ML-CPE, and the observed value of the enrichment factor was 22.8. The standard addition method was used to assess the accuracy and validity of the proposed ML-CPE method of

Fig. 3. Effect of Triton X-114 concentration on pre-concentration of Hg by ML-CPE method using 2.0 µg/L Hg; pH 1.5; 0.25% (v/v); equilibration temperature 45 °C, and time 14 minutes.

Hg at two concentration levels in real groundwater samples (see Table III). Based on the developed ML-CPE/CVAAS method, a recovery of >98% was obtained which confirms the capability and validity of the proposed method. The high enrichment factor and the low LOD of the ML-CPE method suggest that the method is very sensitive and selective for the measurement of Hg in groundwater samples from

the Thar coalfield. The proposed method was satisfactory and comparable to other reported methods (36-39) as is shown in Table IV.

Applications of the Proposed Method

The proposed extraction method was successfully applied for the determination of Hg in groundwater samples of the Thar coalfield, Pakistan. The Tharparkar ground-

water is one of the main sources of drinking water for the local population due to the lack of fresh and pure drinking water throughout the Thar region. The pollution generated from coal mines due to underground gasification results in minerals being dissolved when they come in contact with water. The leaching of Hg due to the use of coal for electricity generation by underground coal gasification may cause the Hg contamination of the groundwater. Since the local population of the Thar area uses groundwater for drinking, most of which is probably collected from underground shallow water sources or well water, it poses a considerable risk of Hg contamination. The results of this study show that the mean value of Hg in the groundwater samples of the Thar coalfield was 2.46 µg/L (see Table III), a value which is above the approved WHO and European Union level of 1.0 µg/L.

CONCLUSION

In this work, a matrix-less cloud point extraction (ML-CPE) procedure is introduced to eliminate matrix effects in the determination of trace levels of Hg in groundwater samples of the Thar coal fields in Pakistan by cold vapor atomic absorption spectrometry. Compared with conventional CPE, the proposed method has extensive application in sample pre-concentration and qualitative analysis of Hg in complex matrices. The proposed ML-CPE method significantly eliminates interference from surfactant, foreign ions, and matrices. With these advantages it offers an extensive application for the pre-concentration step to increase the sensitivity of the spectroscopic detection techniques in complex matrices. The analytical features such as enhancement factor (EF), limit of detection (LOD), and accuracy of the method were satisfactory and comparable to other

TABLE II
Analytical Capability of ML-CPE Method

Concentration range	0.5–10 µg/L
Regression equation (n = 5 (C, µg/L))	Y = 0.1003C + 0.0068
Correlation coefficient	0.9995
LOD ^a	7.50 ng/L
LOQ ^b	25.1 ng/L
Reproducibility (%RSD) ^c (n=10)	4.64 (5 µg/L)
Enrichment factor ^d	22.8

^a Limit of detection. Calculated as three times the S.D. (3σ) of the blank signal.

^b Limit of quantification. Calculated as ten times the S.D. (3σ) of the blank signal.

^c Hg concentration was 5 µg/L for which the %RSD. was obtained.

^d Calculated as the ratio of slope of pre-concentrated samples to that obtained without pre-concentration.

TABLE III
Hg Determination in Real Groundwater Samples by ML-CPE*

Samples	Added (µg/L)	Measured (µg/L)	Recovery (%)
Groundwater	0	2.46 ±0.78	—
	2.0	4.44 ±3.12	99.6
	4.0	6.40 ±3.98	99.1

*Mean ± S.D. (n = 3).

TABLE IV
Comparative Data of Proposed ML-CPE Method for Hg Determination With Conventional CPE Methods

Pre-concentration Method	Concentration Range (µg/L)	RSD (%)	Enrichment Factor	LOD (µg/L)	Ref.
CPE/GFAAS	—	4.0	22	0.01	(35)
CPE/P/ FIA	50–500	4.8	6	0.014	(36)
CPE/CVAAS	—	—	10	0.4	(37)
CPE/CVAAS	10–400	—	—	3.0	(38)
CPE/CVAAS	—	4.6	12	0.117	(39)
ML-CPE/CVAAS	0.5–10	4.64	22.8	0.0075	Present Study

reported methods. The developed ML-CPE method provides useful information for the quantitative determination of Hg in different environmental samples.

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