Arabian Journal of Chemistry (2016) **9**, 105–113

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Simultaneous determination of silver and other heavy metals in aquatic environment receiving wastewater from industrial area, applying an enrichment method

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Received 4 August 2012; accepted 8 October 2014
Available online 25 October 2014

KEYWORDS

Waste water;
Cloud Point extraction;
Heavy metal;
Ammonium pyrrolidinedithiocarbamate;
Flame atomic absorption spectrometry

Abstract In the present study, silver (Ag), cadmium (Cd), nickel (Ni), cobalt (Co) and lead (Pb) were simultaneously determined in water samples of fresh water canal receiving untreated effluents from an industrial area, of Sindh Pakistan. The analytes in the water sample were determined by CPE using ammonium pyrrolidinedithiocarbamate (APDC) as a complexing agent and then entrapped in non-ionic surfactant, octylphenoxypolyethoxyethanol (Triton X-114). The surfactant rich phase was diluted with acidic ethanol prior to analysis by flame atomic absorption spectrometry. The variables affecting the complexation and extraction steps such as pH of sample solution, concentration of oxine and Triton X-114, equilibration temperature and time period for shaking were investigated in detail. The validation of the procedure was carried out by analysis of a certified reference sample of water (CRM1634e). Reliability of the proposed method was also checked by the standard addition method in a real sample at three concentration levels of all metals. Under the optimum conditions, the preconcentration of 10 mL sample solutions, allowed preconcentration

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2014.10.027

factor of 20-fold. The lower limit of detection obtained for Ag, Cd, Ni, Co and Pb was 0.42, 0.48, 0.92, 0.62, and 1.42 μg L^{-1}, respectively. The proposed procedure was successfully applied to waste and fresh water samples for simultaneous determination of different metals. The concentration of Ag, Cd, Ni, Co and Pb has shown a decreased trend from 46.5–6.96, 23.0–8.92, 30.2–12.8, 14.2–4.45 and 15.3–5.32 μg L^{-1}, respectively from initial entrance of waste water along the downstream of canal.

1. Introduction

The contamination of surface water with high level of toxic metals is a matter of serious concern today (Tuzen and Soylak, 2006; Turkmen et al., 2008; Anazawa et al., 2004). Silver (Ag) is both vital and toxic for many biological systems, and its content in environmental samples is increased with the increasing use of its compounds as well as silver-containing products in industry and medicine (Yang and Rose, 2005). In many countries Ag impregnated filters are used for water purification and concentration of up to 50–200 mg L^{-1} of Ag (depending on country) is permitted to control antimicrobial activity with no risk to human health (Tunceli and Turker, 2000). Ag can enter into the environment via industrial waters and might pose a potential risk as water pollutant (Shamsipur et al., 2002).

Cobalt (Co) is known to be an essential micronutrient for metabolic processes in both plants and animals (Sasmaz and Yaman, 2006). It is mainly found in rocks, soil, water, plants, and animals. The determination of trace level of Co in natural waters is very important because Co is important for living species and it is part of Vitamin B12 (Soylak et al., 1997). Exposures to high level of Co lead to serious public health problems and are responsible for several diseases in humans such as, in the lung, heart and skin (Soylak et al., 2001).

Nickel (Ni) is widely used in modern industry. Its overexposure in human beings can provoke significant effects including the lung, cardiovascular and kidney diseases (Zeiner et al., 2007; Ghaedi et al., 2005; Carletto et al., 2009). More attention has been focused on the toxicity of Ni because it can cause allergic reactions and its certain compounds may be carcinogenic (Hirano et al., 2001). Ni with other heavy metals enters in water bodies through natural process from dissolution of rocks and soils, biological cycles, atmospheric fallout, especially from industrial processes and waste disposal production of Ni–Cd batteries and pigments, electronic products, electrodepositing and as catalyst in hydrogenation reactions, which might increase the exposure of this element (Nielsen et al., 1999; Templeton, 1990).

Cadmium (Cd) is highly toxic to human health and damages organs such as the kidneys, liver and lungs (Nordberg et al., 1988). A prolonged intake of Cd leads to a disturbance in the calcium metabolism in biological systems, which induces cell injury and death. It also inhibits the action of zinc enzymes by substitution. Cd is also a teratogenic and carcinogenic agent (Barrera et al., 1997; EPA, 1993).

Lead (Pb) is a toxic metal and it is a widely distributed pollutant in environment. It is an accumulative toxic metal, which produces several diseases, such as hematological disorder, brain damage, anemia, and kidney disorder (Shah et al., 2010). Humans and animals are exposed to Pb from natural as well as anthropogenic sources, e.g. drinking water, soils, industrial emissions, car exhaust, contaminated food and beverages.

A variety of techniques including flame atomic absorption spectrometry (Detcheva and Grobecker, 2008), electrothermal atomic absorption spectrometry (Kiptoo et al., 2008), inductively coupled plasma optical emission spectrometry (Zhu and Alexandratos, 2007), inductively coupled plasma mass spectroscopy (Huang and Hu, 2008) and stripping voltammetry (Zejli et al., 2007) have been extensively used for the determination of heavy metals in different environmental and biological samples. Direct determination of trace amounts of metal ions in samples by FAAS is difficult because of low sensitivity especially of FAAS. Thus, preconcentration procedures are often required (Lee et al., 1997; Ghaedi et al., 2013a,b,c). The cloud point phenomenon has been used in the separation science for extraction, purification and preconcentration of organic and inorganic analytes. This technique is based on the behavior of nonionic surfactants in aqueous solution, which exhibit phase separation by an increase in temperature or by addition of a salting-out agent (da Silva et al., 2001; Quina and Hinze, 1999). Ligands such as dithizone (Manzoori and Karim-Nezhad, 2004, 2003; Manzoori and Bavili-Tabrizi, 2003), 1-(2-pyridylazo)-2-naphthol (PAN) (Cerrato Oliveros et al., 1998; Pinto et al., 1996), ammonium pyrrolidinedithiocarbamate (APDC) (Dadfarnia et al., 2007; Giokas et al., 2001), 1-nitroso-2-naphthol (Manzoori and Bavili-Tabrizi, 2003; Manzoori and Karim-Nezhad, 2003), and 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA) (Safavi et al., 2004) have been employed for cloud point extraction in several procedures for understudy metals. These ligands are widely employed due to several advantages obtained, such as capacity to form complexes with a large variety of metals and low solubility in water. APDC is a classical reagent used for complexing purposes in preconcentration procedures for metals (Giokas et al., 2005).

There is much concern about metal contamination in fresh water bodies of developing countries including Pakistan. The present work is underway to better quantify the addition untreated industrial waste water contains number of contaminant including toxic elements to fresh water bodies. For this purpose the simultaneous preconcentration method was developed and established for preconcentration of trace quantity of Ag, Cd, Ni, Co, and Pb in stream of canal receiving industrial waste water at different distances to evaluate the dilution factor of these toxicants. For the proposed CPE method, ammonium pyrrolidinedithiocarbamate (APDC) was used as a chelating agent and Triton X-114 as non-ionic extractant. The effect of different variables, concentration of complexing reagent, Triton X-114, pH, equilibrium time and temperature were investigated and discussed in detail. The accuracy of the CPE method was evaluated by certified reference material and spiked recovery test. The analyte in the surfactant-rich phase was determined by flame atomic absorption spectrometry (FAAS). The proposed method was successfully applied to real fresh and waste water samples.

2. Experimental

2.1. Chemical reagents and glassware

Ultrapure water obtained from ELGA labwater system (Bucks, UK), was used throughout the work. The non-ionic surfactant, Triton X-114 was obtained from Sigma (St. Louis, MO, USA) and was used without further purification. Stock standard solution of Ag, Cd, Ni, Co, and Pb at a concentration of 1000 µg L^{-1} was obtained from the Fluka Kamica (Bush, Switzerland). Working standard solutions were obtained by appropriate dilution of the stock standard solutions before analysis. Concentrated nitric acid and hydrochloric acid were of analytical reagent grade from Merck (Darmstadt, Germany) and were checked for possible trace levels of Ag, Cd, Ni, Co, and Pb, contamination by preparing blanks for each procedure. Ammonium pyrrolidinedithiocarbamate (APDC) was obtained from Fluka, reagents were prepared by dissolving an appropriate amount of reagent in 10 mL ethanol (Merck) and diluting to 100 mL with 0.01 mol L^{-1} acetic acid. The 0.1 mol L^{-1} acetate and phosphate buffer were used to control the pH of the solutions. The pH of the samples was adjusted to the desired pH by the addition of 0.1 mol L^{-1} HCl/NaOH solution in the buffers. For the accuracy of methodology,

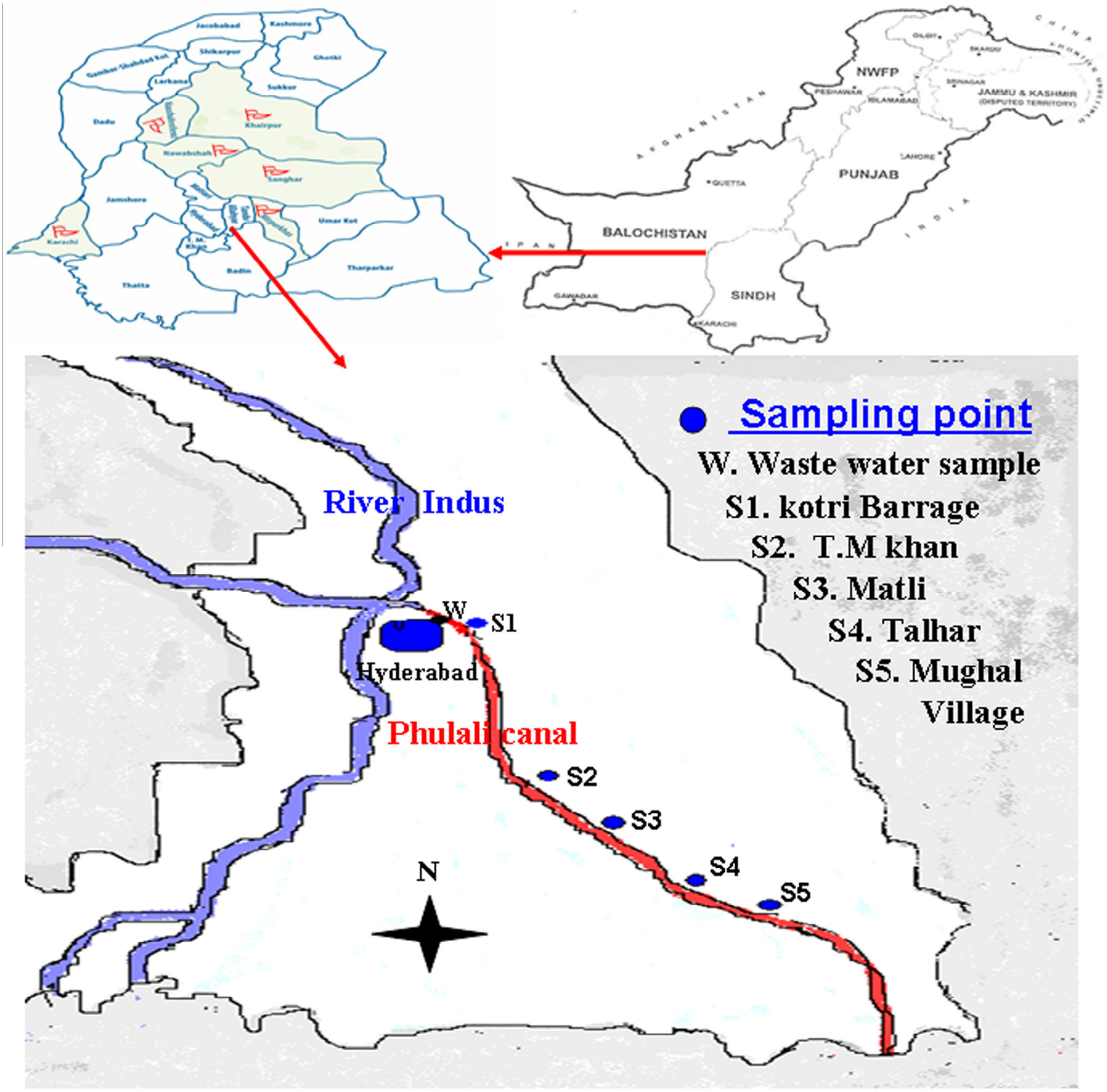


Figure 1 Map showing the six sampling points from upstream (W) to downstream of Phulali Canal (S1–S5).

certified reference material of water (SRM-1643e) National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) was used. The glass and plastic wares were soaked in 10% nitric acid overnight and rinsed many times with deionized water prior to use to avoid contamination.

2.2. Instrumentation

A centrifuge of WIROWKA Laboratoryjna type WE-1, nr-6933 (speed range 0–6000 rpm, timer 0–60 min, 220/50 Hz, Mechanika Precyzyjna, Poland) was used for centrifugation. The pH was measured by pH meter (720-pH meter, Metrohm). Global positioning system (iFinder GPS, Lowrance, Mexico) was used for sampling locations.

A Perkin Elmer Model 700 (Norwalk, CT, USA) atomic absorption spectrometer, equipped with hollow cathode lamps and an air–acetylene burner were used.

2.3. Geographical location of experimental site

A fresh water canal (Phulali) passes through the 2nd big city of the southern area of Pakistan with a population of about 2 million. Most of the municipal and industrial effluents are added to canal water which has a direct impact on the health of human beings, crops and cattle life. Hyderabad city has only two water treatment plants on Phulali Canal. Unauthorized industrial and anthropogenic activates, have further resulted in discharge of solid waste, organic waste, industrial waste, heavy metals, oils and tar in the canal. From the downstream of canal, several towns are present where the population used the untreated water directly from the canal for domestic and agricultural purposes. A survey report from 2006 states that highly toxic effluent from many industries, and sewage water is released into the Phulali Canal (Wattoo et al., 2004).

2.4. Sampling and pretreatment

Water samples were collected in late summer of 2011 from fresh water canal receiving waste water of industrial area at a different point located along the length of the canal (Phulali) and sampling point designated as W, S1–S5 shown in Fig. 1. Water samples were collected in plastic containers previously cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 24 h and finally rinsed with deionised water prior to usage. The waste water samples were collected before and after entering to the canal at different distances (500 m). During sampling, sample bottles were rinsed with sampled water three times and then filled to the brim at a depth of 12 inch from canal water receiving wastewater at different sampling points. All water samples were filtered through a 0.45 micropore size membrane filter paper, to remove suspended particulate matter. The samples were labeled and transported to the laboratory, stored in the refrigerator at about 4 °C prior to analysis.

2.5. Analytical procedure

Cloud point extraction experiment was performed as follows. In a triplicate of each aliquot (10–25 mL) of standards and samples containing the analytes (2–25 μg L^{-1}) were added

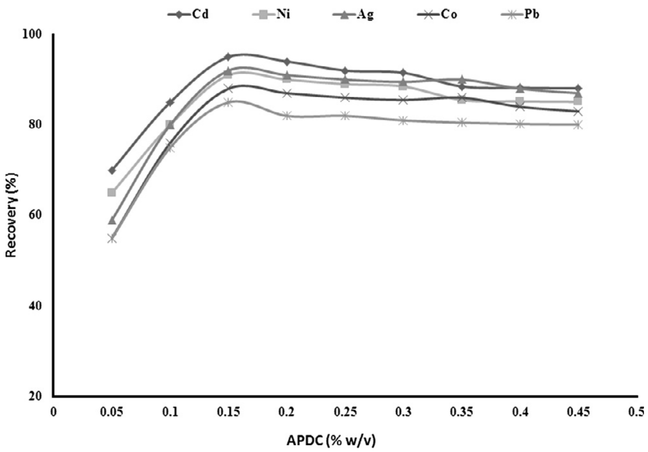


Figure 2 Effect of APDC concentration on the %recovery: 20 μg L^{-1} of Ag, Cd, Ni, Co and Pb, 0.25% (v/v) Triton X-114, pH 5.0, temperature 45 °C, centrifugation time 12 min (4000 rpm).

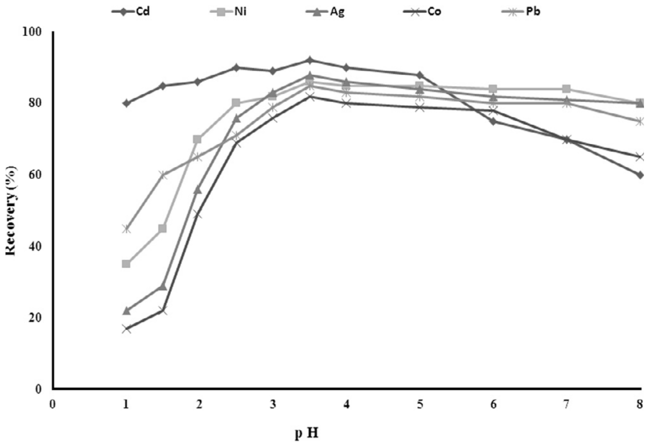


Figure 3 Effect of pH on the %recovery: 20 μg L^{-1} of Ag, Cd, Ni, Co and Pb 0.25% (w/v) APDC, 0.25% (v/v) Triton X-114, Temperature 45 °C, Centrifugation time 12 min (4000 rpm).

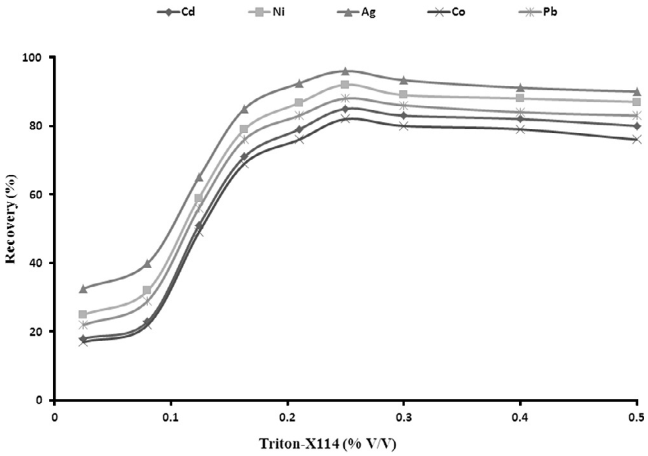


Figure 4 Effect of Triton X-114 on the %recovery: 20 μg L^{-1} of Ag, Cd, Ni, Co and Pb 0.25% (w/v) APDC, pH 5.0, temperature 45 °C, centrifugation time 12 min (4000 rpm).

Table 1 Effect of foreign ions on the preconcentration and determination of silver and other metals (20 μg L^{-1}) on CPE.

Coexisting ions	Interference/ analyte amount
Ba^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, Li^{+}, PO$_4^{3-}$, SO$_4^{2-}$	> 10,000
I^{-}, F^{-}, CO$_3^{2-}$	4000
Cr^{3+}, Fe^{3+}, Zn^{2+}	1500
Al^{3+}	1000
Fe^{3+}, Fe^{2+}	500

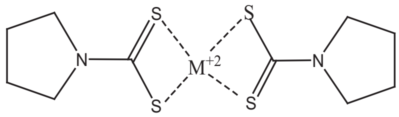
0.1–0.45% (v/v) Triton X-114 solution and APDC (0.05–0.5%, m/v). Subsequently the pH of the solutions was adjusted to the desired values using acetate/phosphate buffer with dilute 0.1 mol L^{-1} NaOH/HNO$_3$ and shaken for 1 min. The tube was left to stand in a thermostated bath for 20 min at 40 °C. Separation of the phases was achieved by centrifugation for 15 min at 4000 rpm. The contents of the tubes were cooled in an ice bath to increase the viscosity of the surfactant-rich phase and the bulk aqueous phase was decanted by carefully inverting the tube. The micellar phase was finally treated with an ethanolic solution containing 0.1 mol L^{-1} HNO$_3$ and left to stand in an ultrasonic bath for 5 min to ensure the complete dissolution of the extracts. The resultant solution was introduced into the flame by conventional aspiration.

3. Result and discussion

3.1. Optimization of CPE

3.1.1. Effect of APDC concentration

The pyrrolidine dithiocarbamate has been widely used as a complexing agent for the extraction and preconcentration of metal ions from aqueous solution. It is a bidentate complexing agent and having ability to form 1:2 metal ligand complex with divalent metal ion. The structure of the metal complex is shown as follows.



The extraction efficiency of Ag, Cd, Co, Ni and Pb as a function of APDC concentrations ranged from 0.05% to 0.45% (w/v) as shown in Fig. 2. The results show that the extraction efficiency of all metals enhances up to 0.15% (m/v). Hence, 0.25% (w/v) of the APDC was selected for quantitative extraction of all the metal ions for further studies. The addition of an excess of chelating agent is required in order to compensate for the its consumption to made complex with other metal ions in sample matrixes. For the present work up to 0.25% of chelating agent was used. The concentrations above this value have no significant effect on the efficiency of CPE.

3.1.2. Effect of pH

The pH plays an important role in metal-chelate formation and subsequent extraction. The enrichment of metal ions by CPE involves the formation of metal–chelate complexes with sufficient hydrophobicity to be extracted in a small volume of nonionic surfactant-rich phase, thus obtaining the desired preconcentration. The effect of sample on the preconcentration of understudy metals was tested in the pH range of 1–8, in the presence of 0.25% APDC and 0.25% Triton X-114 (Fig. 3). Each operational desired pH value was obtained by the addition of 0.1 mol L^{-1} of HNO$_3$/NaOH in the presence of acetate/phosphate buffer. The maximum extraction efficiency of understudy metals was obtained at pH ranges of 2.0–5.5, while slightly decreased at pH range of 5.5–8.0. At low pH (< 2), APDC is decomposed by protonation of the active site pyrrolidine. Protonation determines the rate of decomposition and increased rapidly by lowering pH. Based on these results, pH 5.0 was selected as working value.

3.1.3. Effect of Triton X-114 concentration

The concentration of surfactant that is used in CPE is a critical factor. To obtain the optimal concentration of Triton X-114, the effect of surfactant concentration on the preconcentration of understudy analytes was investigated in the range of 0.05–0.5% (v/v).

The non-ionic surfactant Triton X-114 was chosen as a surfactant due to its low cloud point temperature and high density of the surfactant-rich phase, which facilitate phase separation by centrifugation. Fig. 4 shows that quantitative extraction of all analytes was observed when surfactant concentration was > 0.2% (v/v). At lower concentrations, the extraction efficiency of complexes was low probably because of the inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. A Triton X-114 concentration of 0.25% (v/v) was selected for subsequent study.

Table 2 Analytical characteristics of the proposed method.

Parameters	Ag	Ni	Co	Cd	Pb
Linear range (μg L^{-1})	10–25	10–65	10–25	10–25	10–25
LOD (μg L^{-1})[a]	0.42	0.92	0.62	0.48	1.42
R.S.D. (n = 5)[b]	2.45 (10)[b]	2.18 (15)[b]	2.22 (20)[b]	2.60 (15)[b]	1.88 (20)[b]
Slope	0.0047	0.0034	0.002	0.0039	0.0042
Intercept	0.0416	0.0068	−0.0068	0.0314	0.0073
R^2	0.9994	0.9993	0.9995	0.9865	0.9992
Enhancement factor[c]	47	34	20	39	42

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

[b] Concentration of understudy metals (μg L^{-1}) for which the R.S.D. was obtained.

[c] Calculated as the ratio of slope of preconcentrated samples to that obtained without preconcentration.

Table 3 Determination of silver and other heavy metals in certified reference material and real water samples by standard addition method.

SRM	Certified values (μg L^{-1})					Measured values (μg L^{-1})					Recovery (%)				
	Ag	Cd	Ni	Pb	Co	Ag	Cd	Ni	Pb	Co	Ag	Cd	Ni	Pb	Co
SRM 1643e	1.07 ± 0.08[b]	6.56 ± 0.07	62.4 ± 0.69	19.6 ± 0.21	27.0 ± 0.32	1.05 ± 0.07	6.46 ± 0.07	62.1 ± 0.99	19.2 ± 0.32	26.6 ± 0.30	98.1	98.4	99.5	98.0	98.5
S[a]	Added (μg L^{-1})					Measured (μg L^{-1})					Recovery (%)				
Canal water sample	0	0	0	0	0	19.4 ± 0.95	16.8 ± 0.65	14.9 ± 0.85	8.35 ± 0.98	7.82 ± 0.78	–	–	–	–	–
	2.0	2.0	2.0	2.0	2.0	21.4 ± 1.12	18.3 ± 0.82	16.7 ± 0.81	10.3 ± 0.99	9.8 ± 0.82	98.0	100	98.0	97.5	99.0
	5.0	5.0	5.0	5.0	5.0	24.3 ± 1.20	21.2 ± 0.95	19.8 ± 0.432	13.2 ± 1.12	12.7 ± 0.95	99.0	99.0	98.0	97.0	97.6
	10.0	10.0	10.0	10.0	10.0	12.0 ± 1.32	26.2 ± 0.98	24.6 ± 0.64	17.9 ± 1.22	17.5 ± 0.98	98.0	98.0	97.0	95.5	96.8

[a] Samples.

[b] Mean ± S.D. ($n = 3$).

3.1.4. *Effect of equilibration temperature and time*

The equilibration temperature and the incubation time considered the next important parameters, which has a significant effect on complexation reactions and micelle formation. This can be explained on the basis of the dehydration process that occurs in the external layer of the micelles of non-ionic surfactants when temperature is increased. The dielectric constant of water also decreases by increasing temperature, rendering it a poorer solvent for the hydrophobic portion of the surfactant molecule. It appears that the phase volume ratio of all non-ionic surfactants decreases as the equilibration temperature increases. The greatest analyte enrichment factors are, thus, expected where the CPE is conducted using equilibration temperatures that are above the cloud point temperature of the surfactant. The dependence of extraction efficiency upon equilibration temperature and time was studied in the range of 20–70 °C and 5–30 min, respectively. The results from the optimization experiments showed that an incubation time of 12 min is adequate for quantitative complexation of all metals. The excellent extraction efficiency was achieved for equilibration temperature from 40 to 50 °C. Temperatures above this lead to the decomposition of complexes and the reduction of extraction efficiency. A temperature of 45 °C was used in further experiments.

3.1.5. *Effects of sample volume on preconcentration factor*

The sample volume is one of the most important parameters in the development of the preconcentration method, since it determines the sensitivity and enhancement of the technique. The preconcentration factor (PCF), which is defined as ratio between the original matrix sample volume and the surfactant-rich phase volume. The phase ratio is an important factor, which has an effect on the extraction recovery of cations. A low phase ratio improves the recovery of analytes, but decreases the preconcentration factor. However, to determine the optimum amount of the phase ratio, different volumes of water sample 10–100 mL and a constant volume of surfactant solution 0.25% (v/v) and APDC 0.25% (m/v) was chosen. The obtained results show that with increasing sample volume > 100 mL the extracted understudy analytes decreased as compared to those obtained with 25–50 mL. A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio, thus improving its concentration factor. In the present work the initial sample volume was 10 mL and final volume of the surfactant rich phase after dilution with acidic ethanol was 0.5 mL, hence the PCF achieved in this work was 20 for understudy analytes. As more sample volumes are required in FAAS further experiments were carried out on 25 mL samples while the final volume of the surfactant rich phase after dilution with acidic ethanol was same as given above.

3.1.6. *Interferences*

The interference is that relating to the preconcentration step, which may react with APDC and decrease the extraction. To perform this study, 10 mL solution containing 20 μg L^{-1} of understudy analytes at different interferents to analyte ratio in the presence of Triton X-114 concentration of 0.25% (v/v) was subjected to the developed procedure. The tolerance limit of coexist ions is defined as the largest amount making variation of $< 5\%$ in the recovery of analytes. The effects of representative potential interfering species were tested. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes under the experimental conditions. A high concentration of APDC reagent was used, for the complete chelation of the selected ions in the presence of interferent ions. Table 1 shows the tolerance limits of the interfering ion error $< \pm$ 5%.

3.1.7. *Analytical figures of merit*

The linear range, detection limits, relative standard deviations and enhancement factor obtained under the optimized conditions of extraction are listed in Table 2. The precision of the method was checked by calculating the relative standard deviation (RSD) on five standard solutions containing the analytes. The limits of detection (LOD) are the lowest analyte concentration that produces a response detectable above the noise level based on 3 times the standard deviations of the blank. Under the optimized conditions a detection limit of 0.42, 0.48, 0.92, 0.62 and 1.4 μg L^{-1}, along with enrichment factors of 47, 39, 34, 20 and 42 for Ag, Cd, Ni, Co and Pb, which were calculated from the ratio of the slopes of the calibration graphs with desired method and without preconcentration method. It should be mentioned that the enrichment factor of our method can be improved by using larger volumes of initial sample solutions. Validity and accuracy of the proposed method were checked by applying it, to the standard reference material, NIST SRM 1643e (Trace elements in water). The obtained value by using the proposed CPE method is in good agreement with the certified values in Table 3, which indicated that the proposed method is accurate and free from systematic errors. Reliability of the proposed method was also checked by spiking standards of understudy metals at three concentration levels (2.0–10.0 μg L^{-1}) in a real water sample as shown in Table 3. The recovery% (R) of spike standards was calculated as follows:

$$R(\%) = \frac{(C_m - C_o)}{m} \times 100$$

where C_m is a value of metal in a spiked sample, C_o is the value of metal in a sample, and m is the amount of metal spiked. As can be seen from Table 3 that recoveries between 97% and 100% were obtained, which again confirm the accuracy and validity of the proposed method.

3.1.8. *Application to real samples*

Our objectives in this study were to determine how metal concentrations varied spatially along the length of the Phulali Canal after addition of treated and untreated effluents in fresh water body. The concentration of understudy metals were transformed into standard unit (z) to compare the aspects of the variation in water samples collected from different sites along the canal. The average concentrations of understudy metals in waste water effluent measured at entering (W) and subsequent sampling points as shown in Table 4. This simple estimation highlights the fact that industrial discharged effluent can supply a considerable quantity of toxic metals into the receiving canal. As shown in Fig. 5 and Table. 4 the concentration of silver and understudy heavy metals has shown a decreased trend from S1 to S5 downstream in the following order W > S1 > S2 > S3 > S4 > S5. This variation in concentration levels of heavy metals in different downstream sampling points is due to sedimentation, dilution and effective removal processes such as e.g., adsorption/desorption, oxidation/reduction, biological uptake/regeneration. The concentration of understudy metals was transformed into standard unit (z) to compare the aspects of the variation in concentration of water samples collected from different sites along the canal as shown in Fig. 5. Silver and other understudy metal ions were high at entering point of waster water coming through different routes. The silver and other heavy metals show low normalized values at site 4 and 5 (below 0), whereas the values of these analytes are higher at entering point (w) equivalent to their mean values above two standard deviation (2s). The values of all heavy metals at site 3 shows slight variation, the values of Ag and Ni are < 0 while other three heavy metals, Co, Pb and Cd are > 0. The concentration of understudy heavy metals in waste effluents and after mixing with fresh water up to different site was above at sampling point (S3) than acceptable limits for potable waters according to WHO and EPA, which could be estimated that the study area is much polluted and creates continuous hazardous impacts on consumers (human and animals) and crops.

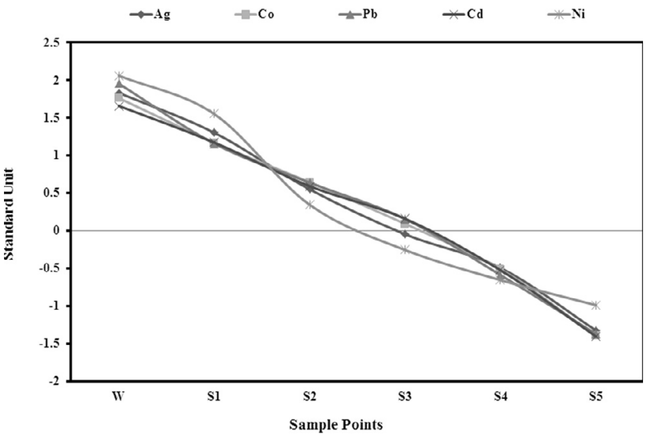


Figure 5 Standard unit concentrations of silver and other heavy metals in water of Phulali Canal. The standard units is defined as $z = (x - u)/S$, where x is the raw concentrated data, u is the mean values and S is the standard deviation.

Table 4 Concentration of heavy metals (μg L^{-1}) at the waste water site and at different sampling points of Phulali Canal.

Metals	W	S1	S2	S3	S4	S5
Ag	54.4 ± 2.52	46.4 ± 2.32	35.2 ± 1.55	26.2 ± 1.12	19.4 ± 0.95	6.96 ± 0.85
Cd	25.6 ± 1.23	23.0 ± 1.12	20.0 ± 0.98	18.4 ± 0.75	16.8 ± 0.65	12.9 ± 0.62
Ni	33.6 ± 1.85	30.2 ± 1.45	26.4 ± 1.12	18.5 ± 0.98	14.9 ± 0.85	12.8 ± 0.75
Co	16.5 ± 1.12	14.2 ± 1.02	12.2 ± 0.98	10.1 ± 0.82	7.82 ± 0.78	4.45 ± 0.75
Pb	18.5 ± 1.45	15.3 ± 1.23	13.2 ± 1.14	11.3 ± 1.02	8.35 ± 0.98	5.23 ± 0.85

Table 5 Characteristic performance of the developed CPE method with previously reported methods.

Metals	Reagent	Surfactant	PF	LOD (μg L^{-1})	Refs.
Cd	DDPH	Triton X-114	10.5	0.95	Ojeda et al. (2010)
Cd	TAN	Triton X-114	20.3	–	Talebi et al. (2007)
Ni	PAN	Triton X-114	25	6.0	Cerrato Oliveros et al. (1998)
Ni	APDC	Triton X-114	20	11.0	Giokas et al. (2001)
Co	APDC	Triton X-114	20	5.0	Giokas et al. (2001)
Pb	DDTP	Triton X-114	43	2.86	Manzoori and Bavili-Tabrizi (2002)
Pb	–	PONPE 7.5	10	–	Luconi et al. (2000)
Ag	(MBT)	Triton X-114	46	2.2	Shemirani et al. (2007)
Ag	(BMAA)	Triton X-114	50	0.43	Shemirani et al. (2006)
Cd	APDC	Triton X-114	39	0.48	Present work
Ni	APDC	Triton X-114	34	0.92	
Co	APDC	Triton X-114	20	0.62	
Pb	APDC	Triton X-114	42	1.42	
Ag	APDC	Triton X-114	47	0.42	

3.1.9. Comparison of CPE with previously reported methods

The proposed CPE method has been compared with previously reported methods (Table 5). The simultaneous determination of multi elements (Ag, Co, Cd, Pb and Ni) by a single step cloud point extraction procedure highlighted the capability and feasibility compared with other methods. Table 5 shows that our proposed method has high enrichment factors and low detection limits for studied analytes. This method can be easily used for routine analysis of trace quantities of more heavy metals in different environmental samples.

4. Conclusion

The proposed method enables the simultaneous determination of trace quantities of Ag, Co, Cd, Pb and Ni with a single step cloud point extraction in combination with FAAS. The method utilizes the solubilization ability of non-ionic surfactant micelles (Triton X-114) to entrap and isolate hydrophobic metal chelates produced from the reaction of the metallic ions with APDC under the optimum experimental conditions. The Ag, Co, Cd, Pb and Ni in different industrial waste water (W1) contaminating the fresh water canal and showed spatial variation in decreasing trends to downstream (S1–S5). This is the first study to provide evidence on the influence of industrial effluent on silver and heavy metal concentration in the receiving fresh water canal, which is a lifeline of a large number of population, animal farm houses and agricultural lands. Our results indicated that the spatial distribution of studied metals in the downstream water appears to be lowered by the dilution effect of canal runoff and background-eroded sediments, apart from the strength of pollution sources. This also highlights potentially substantial effects on the aquatic ecosystem and establishing fundamental data on the specific heavy metal pollution profiles of each type of industrial activity. The resulted data of the present study enable identification of pollution sources for the formulation of management strategies.

Acknowledgments

The authors would like to thank National centre of excellence in analytical chemistry (NCEAC) university of Sindh Jamshoro for providing financial support and excellent research lab facilities for scholars to carryout research work.

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