SEPARATION, PRECONCENTRATION, AND DETERMINATION OF LEAD, CADMIUM, AND IRON USING CLOUD POINT EXTRACTION WITH FLAME ATOMIC ABSORPTION SPECTROMETRY**

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The concentration of heavy metals in drinking water is an important standard for water quality evaluation and water pipeline corrosion detection. This research reports the development of a new method based on cloud point extraction for the separation, preconcentration, and detection of lead (Pb), cadmium (Cd), and iron (Fe) using flame atomic absorption spectrometry. This method was used because the concentration of metallic trace elements in the samples was lower than the limits of detection (LOD). The experimental LODs for Pb, Cd, and Fe, were 0.01, 0.01, and 0.3 ppm respectively, which were determined based on a significant sensitivity change in the slope of the standard curve. By using both 2,6-diamino-4-phenyl-1,3,5-triazine and 3-amino-7-dimethylamino-2-methylphenazine (Neutral Red) as chelating agents, and Triton X-114 as a surfactant, these metallic elements were enriched in water samples. The preconcentration procedure was optimized by varying the experimental factors such as temperature, equilibrium time, pH, and the concentration of the chelates and surfactant. After optimization, this method allowed the determination of these three trace elements with 20-times lower LODs and yielded recoveries of 99.8, 97.3, and 99.3% for Pb, Cd, and Fe, respectively.

Keywords: *preconcentration, cloud point extraction, heavy metals.*

РАЗДЕЛЕНИЕ, КОНЦЕНТРИРОВАНИЕ И ОПРЕДЕЛЕНИЕ СВИНЦА, КАДМИЯ И ЖЕЛЕЗА С ИСПОЛЬЗОВАНИЕМ ЭКСТРАКЦИИ В ТОЧКЕ ПОМУТНЕНИЯ И ПЛАМЕННОЙ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ

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Разработан метод для обнаружения и определения предварительной концентрации свинца, кадмия и железа, основанный на экстракции в точке помутнения, с использованием пламенной атомно-абсорбционной спектрометрии. Метод применен при концентрации металлических микроэлементов в образцах ниже пределов обнаружения (LOD). Экспериментальные LOD 0.01, 0.01 и 0.3 ppm для Pb, Cd и Fe, соответственно, определены на основе значительного изменения наклона стандартной кривой. С использованием 2,6-диамино-4-фенил-1,3,5-триазина и 3-амино-7-диметиламино-2-метилфеназина (нейтрального красного) в качестве хелатообразующих агентов, а также Triton X-114 в качестве сурфактанта пробы воды обогащались элементами металлов. Процедура предварительного концентрирования оптимизирована путем изменения экспериментальных факторов, а именно температуры, времени равновесия, pH и концентрации хелатов и поверхностно-активного вещества. После оптимизации метода микроэлементы определены в следо-

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вых количествах с 20-кратным снижением пределов обнаружения и извлечением 99.8, 97.3 и 99.3 % для Pb, Cd и Fe соответственно.

Ключевые слова: *предварительная концентрация, извлечение точки помутнения, тяжелые металлы.*

Introduction. Heavy metals and metalloids in drinking water have long been considered potential threats to public health owing to their long-term toxicity for humans. As the most toxic heavy metal listed by the United States Environmental Protection Agency (USEPA), lead (Pb) is associated with a wide range of neuropsychological deficits and metabolic disorders by the National Academy of Science (NAS) [1]. Cadmium (Cd) is another heavy metal that is extremely difficult for the human body to eliminate by regular physiological metabolism. According to a World Health Organization (WHO) report, the half-life of Cd stored in an adult's kidney and liver is between 10 and 35 years, only a small part of which (about 0.07%) can be excreted through the urine. Unlike Pb and Cd, Fe is a trace element that may not directly pose health concerns to humans [2]; however, the scale formed on the inner surface of water pipelines may reduce their cross-sectional area, which may reduce the water-head. The released suspensions of Fe particles may also give drinking water an unappealing red color.

Based on the requirements of the Safe Drinking Water Act (SDWA), the USEPA established the National Primary Drinking Water Regulations (NPDWRs) and Secondary Drinking Water Standards, which specify the limits for the amounts of heavy metals in public water systems. According to these regulations, the maximum contaminant levels (MCLs) of Pb, Cd, and Fe are 15, 50, and 300 mg/L, respectively; however, it is difficult to accurately determine the concentration of heavy metals in water using only regular analytical chemistry instruments, such as flame atomic absorption spectrometer (FAAS) as the LODs are usually much higher than sample concentrations (Table 1). Therefore, to ensure water quality compliance with EPA standards and the accuracy of heavy metal measurements, a sample preconcentration process is required before FAAS detection.

TABLE 1. USEPA Drinking Water Standards Concerning Lead, Cadmium, and Iron

Contaminants	EPA Standards		Detection limit of FAAS, mg/L
	MCLG [a], mg/L	MCL [b], mg/L	
Lead	0	0.015	0.1
Cadmium	0.005	0.005	0.1
Iron	0.3	0.3	0.5

[a] Maximum contaminant level goals according to USEPA standards.
[b] Maximum contaminant levels.

Much research has been conducted concerning the preconcentration of heavy metals in environmental samples by using chelating resins synthesized with ion-selective ligands and polymer resins [3–7]. For instance, Mahmoud et al. [4] developed a method of separating multiple heavy metals including Au(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), Pd(II), and Zn(II) from aqueous solutions by using chloromethylated polystyrene-PAN (CMPS-PAN) ion-exchanger. This method showed high preconcentration recoveries for Co, Cr, Cu, Fe, Mn, Pd, and Zn. Similarly, Liu and colleagues utilized Dowex 50WX8 strong acid cation-exchange resin to perform the solid-phase extraction of multiple metallic elements from water samples [7]. When using direct detection with ICP-MS, the results were basically identical, and the method had high accuracy [7]; however, with such methods, the chelating resins required a time-intensive preparation procedure (e.g., PAN required at least 168 h) owing to a complicated synthesis procedure that included chain-transfer, copolymerization, and crosslinking reactions [6]. Additionally, the physicochemical properties of the resin were usually uncontrollable, including its specific surface area, surface charge, porosity, and hydrophilicity, which may significantly influence the absorption capacity and preconcentration recovery.

Cloud point extraction (CPE) is a pretreatment method for the separation and preconcentration of metallic analytes before analytical quantification using less-sensitive instruments such as FAAS [8–11]. This process separates aqueous solutions into two isotropic phases by changing the physical conditions such as tem-

perature and pressure. As the temperature of a solution rises, the surfactant molecules usually include a long hydrophobic hydrocarbon chain, and a small charged headgroup or a polar hydrophilic headgroup gradually forms micelles. Once the temperature increases above the cloud point (CP), the micelles become dehydrated and aggregate (Fig. 1). This leads to macroscopic phase separation of the solution into a surfactant-rich phase and a solvent phase, which traps the organic/inorganic analytes in micelles that can be extracted for later measurements. Compared with the previously mentioned methods, CPE is an easy, quick, accurate, and environmentally safe method with costs, no secondary contamination, toxicity, or volatility.

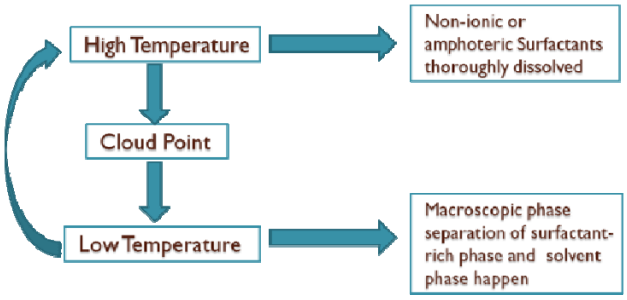


Fig. 1. Principle of cloud point extraction.

TABLE 2. Preconcentration of Metallic Trace Elements by CPE

Matrix	Elements	Reagent/Surfactant	Preconcentration factors	Technique	Ref.
Water sample	Cd	PAR/Triton X-114	9.4	ICP-OES	[10]
Environmental sample	Cd, Pb, Pd, Ag	BIES/Triton X-114	30	FAAS	[12]
Water sample	Cd	O-phen and eosin/PONPE 7.5	–	Molecular fluorescence	[13]
Rice & water	Cd	Dithizone/Triton X-114	152, 93	W-coil ETV-AFS & W-coil ET-AAS	[14]
Water & food sample	Cd, Cu, Ni, Pb	BNBATT/Triton X-114	100	FAAS	[15]
Water & food sample	Cd, Cu, Co, Ni, Pb	BTAAP/	100	multi-walled carbon nanotubes & FAAS	[16]
River & tap water	Se	Toluene/DAB	10	UV-Vis & fluorescence	[17]
Food sample	Na, Cu	Triton X-114	–	UV-spectrophotometer	[18]
Water sample	Ag, Cd, Ni	Dithizone/Triton X-114	41-58	FAAS	[19]
Water sample	V	8-HQ & $[C_4mim][PF_6]$	100	GFAAS	[20]
Water & food sample	Se	Triton X-114/$BMImPF_6$	20	FAAS	[21]
Water & food sample	V	ZnCl, Acetamide/Triton X-114	64.6	GFAAS	[22]

Much research based on CPE has been reported in the past 20 years (Table 2). Chelates and surfactants are often used to trap metallic trace elements and perform liquid-liquid or solid-liquid phase separation. The preconcentration recoveries of these methods are often strongly dependent on the type of elements when multiple analytes are present in a sample, making it difficult to obtain satisfying recoveries for all elements [12, 15, 16]. Additionally, accessories may be required for sample pretreatment and mixing, such as multi-walled carbon nanotubes [16] and flow injection systems.

Citak and Tuzen introduced a CPE method for the preconcentration of Cu, Ni, Pb, Cd, and Fe. This method utilized 2,6-diamino-4-phenyl-1,3,5-triazine (DPT) for chelation, and an amphiphilic organic surfactant, Triton X-114. The solubility and activity of non-ionic surfactants depend on the hydrophilic ether link-

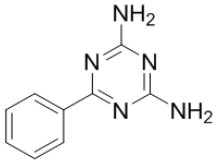
ages in the polyoxyethylene chain (Triton® X Surfactants). Triton X-114 is soluble at room temperature, but as the temperature increases, its solubility decreases. The "cloud point" is the temperature above which the solution becomes turbid and two phases are formed [23, 24]. Dissolved inorganic salts have a similar effect on the surfactant's solubility in water, as does the temperature. Because dissolved salts have a greater affinity for water than the ether linkages, they can dehydrate the non-ionic compound, resulting in the replacement of hydrogen atoms in the amino groups with metal ions; however, the maximum recovery for Fe is only 83% (Table 3) [23].

TABLE 3. Methodology Comparison of CPE Using Only FAAS

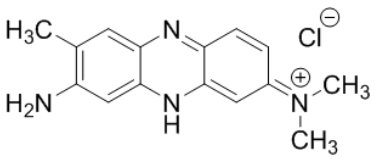
Optimal conditions for iron preconcentration	Triton X-114 & DPT (Citak and Tuzen, 2010)	Triton X-114 & NR (Sahin, et al., 2010)
pH	8.5	7.0
Concentration of chelating Agent	0.1% (w/v)	0.1% (w/v)
Concentration of surfactant	0.4% (v/v)	0.05% (v/v)
Equilibrium temperature,°C	70	50
Equilibrium time, min	20	30
Recovery according to literature (%)	97.0 with FAAS	98.7 with FAAS & FIS
Recovery (%)	83 (with FAAS)	75 (only with FAAS)
RSD	1.7–4.8% (n = 7)	1.8–2.1% (n = 10)
Preconcentration factor	25	69–98

In another example, Sahin and co-workers developed a new method for the preconcentration and determination of Fe in patient's blood using Triton X-114 and 3-amino-7- dimethylamino-2-methylphenazine (Neutral Red, NR) with CPE and a flow injection system for FAAS [24]. NR is utilized as a stain and counterstain in medical applications, and is strongly dependent on pH [24]. The recoveries of the method reported by Sahin were no lower than 98%, but a flow injection system (FIS) was required for sample loading, separation, and elution. Flow injection analysis (FIA) is based on the injection of a liquid sample into a moving, nonsegmented continuous carrier stream of a suitable liquid. The injected sample forms a zone that is then transported toward a detector that continuously records changes in the absorbance, electrode potential, or other physical parameters resulting from the passage of the sample through the flow cell. Many studies have shown that FIS is an easier and more versatile system with greater recovery and reproducibility for heavy metal preconcentration, compared with the traditional batch methods. Moreover, FIS can enhance the preconcentration factor of samples from an original value of 20–25 to 50, or even 70, to make the sample concentration fall completely within the detection range of an instrument. Unfortunately, flow injection is an uncommon accessory that is not usually available in most chemistry laboratories. In this research, centrifugation methods were tested without a flow injection system, but the recoveries using centrifugation are typically only around 75%.

Owing to the advantages and disadvantages of the methods mentioned above (summarized in Table 4), this research developed a new method for the preconcentration of metallic trace elements in water samples by using multiple chelating reagents. To obtain a high recovery and reproducibility, experimental factors were optimized, including the temperature, equilibrium time, pH, and the concentration of the chelates and surfactant.



DPT structure



Neutral Red structure

TABLE 4. Comparison of Preconcentration Methods

Preconcentration methods	Advantages	Disadvantages
Ion-exchange	1. High recovery 2. High reproducibility 3. Hydrogel can be recycled	1. Synthesis of ion-exchangers is complicated and requires long-term preparation 2. Ion-exchanger recycling may cause secondary contamination
AC + chelating agent	1. Procedure is simple and quick	1. Preconcentration recoveries are low for certain elements 2. Physical adsorption ability of AC is limited compared with ion-exchange hydrogel
Cloud point extraction	1. Procedure is simple and quick 2. Recovery and reproducibility are relatively high	1. May require additional accessories 2. Chelating reagents are selective for metallic trace elements 3. Surfactant phase is easy to disturb during phase separation

Materials and methods. *Chemicals.* The chemicals used in this research were purchased from Sigma-Aldrich (St. Louis, USA) at the highest purity available and used as received. DPT stock solution was prepared by dissolving 0.2 g of DPT in 30.0 mL methanol (99%) and then diluting to 100 mL by double distilled water at 70°C. An NR stock solution was prepared by dissolving 0.1 g of NR (≥90%) in 100 mL of double-distilled water. The calibration standards and the spike solution were prepared by using iron(III) chloride (1000 ppm, ≥99.99%) standard solution, lead(II) nitrate standard solution (1000 ppm, ≥99.99%), and cadmium(II) nitrate stock solution (1000 ppm, ≥99.99%). The buffer solution with a pH from 4 to 7 was obtained by diluting an appropriate amount of acetic acid (≥99.5%) and sodium acetate (≥99.0%) with distilled water. The buffer solution of pH 8–12 was prepared by titrating an appropriate amount of ammonium hydroxide solution (~28–30%) and NH4Cl (99.99%) with distilled water.

Apparatus. An Analyst 400 flame atomic absorption spectrophotometer (PerkinElmer, Waltham, USA) with an air-acetylene flame and auto-sampler (PerkinElmer, Waltham, USA) was used to determine Fe concentration. The flow rates of gases were optimized. The analytical wavelengths were 248.3, 217.0, and 228.8 nm, respectively, for Fe, Pb, and Cd. All other experimental parameters were set at the system-recommended values. A waterproof pH meter (Oakton, Vernon Hills, IL, USA) with ±0.1 accuracy was utilized to determine the pH of each solution. A Grant JBA5 (Cambridge, UK) basic unstirred water bath was used for incubation. A VWR (Chicago, IL, USA) mini vortex (120 V) was employed for sample mixing.

Experimental. We followed and further improved upon the method of A. Rihana-Abdallah et al. [25] by optimizing the experimental factors. Standard and spike solutions of iron(III) and lead(II) were prepared by diluting 1000 ppm $FeCl_3$ and $PbCl_2$ stock solution, respectively. The final concentrations of the calibration standards of Fe were 0.5, 1.0, 1.5, 2.0, and 2.5 ppm. The final concentrations of the Pb and Cd calibration standards were 0.1, 0.2, 0.3, 0.4, and 0.5 ppm, respectively. The correlation coefficients of Fe and Pb detection were both higher than 99.99%, as tested by FAAS. The concentrations of Fe spike solutions ranged from 0.0 to 1.0 ppm with an increase of 0.1 ppm. Similarly, the concentration of Pb and Cd spike solutions ranged from 0.00 to 0.20 ppm with an increase of 0.05 ppm. The absorption signals for each spike solution as well as the blank were detected by FAAS. The results indicated that 0.5 ppm was the lowest concentration level that can be determined to be statistically different from a blank with a 99% confidence level for Fe. Similarly, 0.1 ppm was the lowest detection level for Pb and Cd using FAAS.

A 100-mL sample solution contained 0.025 ppm of Fe stock solution, 0.005 ppm of Pb stock solution, 0.005 ppm of Cd stock solution, 2.0 mL of NR stock solution, 0.2 mL of 99% Triton X-114, and 2.5 mL of DPT. This solution was buffered to pH 8.0 and incubated at 70°C for 25 min (optimal equilibrium time). After 20-min centrifugation (VWR clinical 200 centrifuged at 3800× g), the sample solution was exposed to an ice bath for 15 min, and then the aqueous phase was separated from the surfactant phase by careful pipetting. The surfactant phase remaining at the bottom of the centrifuge tube was dissolved in 5 mL of 1 M nitric acid in methanol. After mixing for 5 min, the sample solution was tested by FAAS, along with the standard solutions. The blank samples were prepared and treated using the same approach as above, but without an analyte.

The preconcentration process yielded a 5-mL sample that was adequate for FAAS detection without an installed FIS. Moreover, the reduction of the sample volume from 100 to 5 mL increased the sample concentrations by 20 times from 0.005 to 0.1 ppm for Pb and Cd, and from 0.025 to 0.5 ppm for Fe, which are higher than the FAAS detection limit, allowing them to be accurately measured. The purpose of this study was to ensure that the levels of trace elements in drinking water samples complied with the USEPA drinking water standards (0.015, 0.005, and 0.3 ppm for Pb, Cd, and Fe respectively; thus, we selected the initial concentrations of 0.025, 0.005, and 0.005 ppm for preconcentration by CPE to prove the efficacy of the method.

Results and discussion. In environmental or food samples, the signal of the analytical targets often experiences interference owing to the presence of other trace elements, which is called spectral interference. Spectral interference can increase the light absorption of an analyte when using spectroscopic methods. In this research, the mutual influence of Pb, Cd, and Fe, as well as other metallic trace elements, including Zn, Na, Mg, and Ni, were investigated before applying this preconcentration method for water samples. The results indicated that the effect of other trace elements on the analytical signals of Pb, Fe, and Cd was negligible, even when the concentration reached 100 ppm. With the optimization of the pH, temperature, and concentration of chelating agents and surfactants, the maximum preconcentration recoveries for Pb, Cd, and Fe reached 99.8, 95.9, and 99.3%, respectively. These values were calculated as the ratio of the measured sample concentration over the theoretical sample concentration. The data points in Figs. 2–6 represent the average preconcentration recoveries of five replicates for each sample group.

Effect of temperature on recovery. The temperature during CPE can significantly affect coordination reactions and micelle formation [25]. A high temperature increases the solubility of DPT and NR in water, and also enhances the probability of collisions between metal ions and chelating reagents. A high temperature also allows surfactants to mix more thoroughly with the insoluble conjugates formed by the metallic trace elements and chelates, increasing the removal efficiency. A reasonable explanation of this principle is that when the temperature increases, the water molecule layer surrounding the surfactant molecules is destroyed owing to an increase in entropy. The week Van der Waals forces between the molecules lead to the agglomeration of micelles.

As illustrated in Fig. 2a, the percentage recovery increased dramatically when the equilibrium temperature increased from 40 to 50°C. Temperatures within this range are much higher than the cloud point of Triton X-114 (around 23°C) [26]. Such high temperatures allow the surfactant to fully dissolve in the matrix, and dehydration rapidly occurred in the exterior layer of the Triton X-114. Above 70°C, the recoveries for Pb, Cd, and Fe plateaued without further increasing; therefore, the equilibrium temperature of 70°C was the optimal temperature and was applied to the rest of the experiments.

The bars in Figs. 2 and 3 represent the standard deviation of the mean that was calculated based on five repeated measurements of each sample. The experimental parameters utilized for the optimization of equilibrium temperature (pH, concentration of chelating reagents and surfactant, equilibrium time and centrifuge rate) are listed in Table 4 (also applied to Figs. 2b and 3).

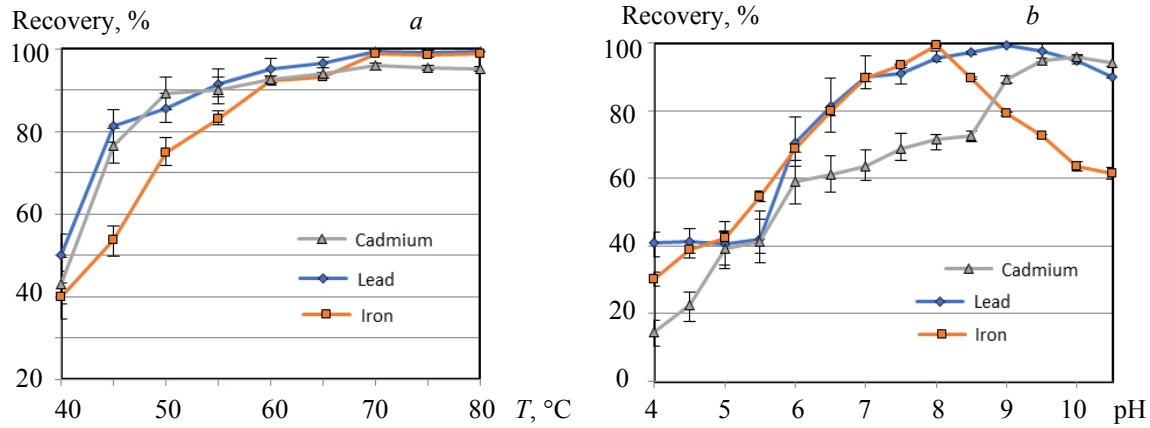


Fig. 2. Effect of temperature (a) and pH (b) on recovery.

Effect of pH on recovery. The pH can significantly influence the activity of chelating agents. In an acidic environment, metallic trace elements have difficulty competing with hydrogen ions for the binding sites of chelating reagents, but at a higher pH, the coordination product formed between heavy metal ions and ligands becomes more stable than that formed by hydrogen ions. The binding capacity eventually reaches a peak at the optimal pH. As the experimental data in Fig. 2b show, the optimal pH values for the preconcentration of Fe, Pb, and Cd were 8.0, 9.0, and 10.0, respectively, which were used for subsequent experiments.

Effect of surfactant concentration on recovery. Triton X-114 is one of the most widely employed nonionic surfactants for the separation and preconcentration of heavy metals using cloud point extraction. It is a homogeneous solution at 0°C but has a cloud point of around 23°C. Owing to this feature, mixtures of Triton X-114 and the hydrophobic complex of chelating agents and metal ions can be removed from aqueous solutions by phase separation. It is necessary to optimize the surfactant concentration, as too little surfactant cannot fully entrap and precipitate all coordination products from aqueous samples. On the other hand, too much surfactant may reduce the enrichment rate (initial sample volume/final sample volume after phase separation), and can also decrease the sensitivity of the FAAS measurements owing to a higher sample viscosity. As illustrated in Fig. 3a, the recoveries increased significantly when the surfactant concentration was between 0 and 0.2% (mL/100 mL), and then began to drop and fluctuate. Therefore, 0.2% (mL/100 mL) was selected as the optimal Triton X-114 concentration for the remaining experiments.

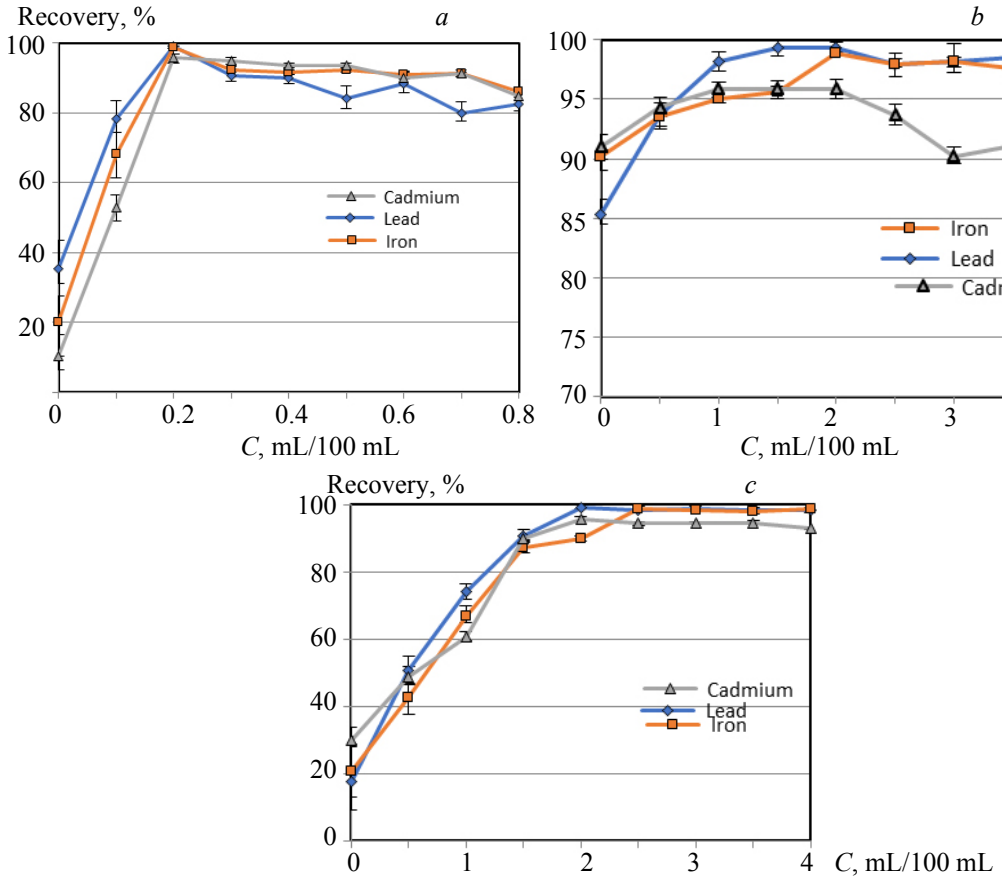


Fig. 3. Effect of concentration of Triton X-114 (a), NR (b), and DPT (c) on recovery.

Effect of chelating agent concentration on recovery. Optimizing the dosage of chelating reagents can enhance the extraction efficiency. In this work, DPT was the main chelating agent, which conjugated with metal ions by replacing the hydrogen atom of the amino group to form a hydrophobic product. Neutral Red was a secondary chelating agent that further enhanced CPE efficiency by adding a much smaller amount than DPT; thus, it is necessary to optimize the concentrations of chelates because redundant chelating reagents in the matrix may reduce the solubility and decrease CPE efficiency. Additionally, the concentration ratio of DPT to NR played an important role in CPE. The results of this research suggested that the optimal

ratio was between 10 and 20. Figure 3b illustrates the change in recoveries as the addition of NR increased from 0 to 0.4 mL/100 mL. The optimal concentration of NR for Cd was determined to be 0.1 mL/100 mL and that of Pb and Fe was 0.2/100 mL. These optimized factors were utilized for the remaining experiments.

The effect of DPT concentration on CPE recovery is shown in Fig. 3c. In the absence of DPT, the preconcentration efficiency was only around 20% for Pb, Cd, and Fe. The recoveries for Cd and Pb were dramatically improved and reached their highest levels when the concentration of DPT increased from 0 to 2.0 mL/100 mL, and remained stable after that. Similarly, the highest CPE efficiency for Fe was observed when the concentration of DPT reached 2.5 mL/100 mL; thus, the optimal concentrations of DPT for the cloud point extraction of Pb, Cd, and Fe were 2.0, 2.0, and 2.5 mL/100 mL, respectively.

Effect of equilibrium time on recovery. After adding chelating reagents and surfactants, the water samples were placed in a water bath at 70°C to fully dissolve Triton X-114 and accelerate the coordination reaction. The equilibrium time needs to be optimized as the dissolution of Triton X-114 and the coordination between ligands and analytes will be incomplete if it is too short. On the other hand, excessive temperature may lead to the decomposition of coordination complexes and a reduction in the CPE recoveries and reproducibility. In this research, the dependence of extraction efficiency on the equilibrium time was explored within the range of 10–40 min. The results indicated that 25 min was the optimal equilibrium time.

Effect of sample volume on recovery. After preconcentration, a treated sample matrix usually consists of a surfactant-rich phase, as well organic and/or inorganic solvents, such as methanol, ethanol, hydrochloric acid, and nitric acid. In this research, the volume of the surfactant-rich phase obtained after phase separation was around 1 mL. As the surfactant, Triton X-114, easily dissolves in organic solvents, a HNO_3-methanol mixture of around 1–1.5 mL is sufficient; however, without a flow injection system, the preconcentrated aqueous sample with a final volume of 2–2.5 mL was unable to provide the FAAS with a continuous and well-mixed sample flow. To obtain the highest sensitivity and accuracy for measuring metallic trace elements, the FAAS nebulizer must be adjusted by comparing the absorbance of the copper standard solution with the spectral absorption standard recorded in the instruction manual. The sample flow rate is often set to a high level to allow more sample to flow through a nebulizer and reach the torch. Usually, the sampling procedure includes at least 3-s reading time and 12-s detention time to yield a series of reliable readings with a high correlation coefficient; therefore, such a low-volume sample may not withstand 15-s suction at that flow rate, not to mention up to five repeated measurements. Thus, the sample readings may be very unstable, with a high standard deviation and low correlation coefficient. In this research, the minimum volume of the final aqueous sample that could generate stable sample readings with high reproducibility and recoveries was around 5 mL, according to the FAAS measurements.

Effect of centrifugation time on recovery. Centrifugation was applied to the water sample immediately after removal from the ice bath. To fully precipitate the surfactant phase from the sample matrix, the effects of centrifugation time and rates on the CPE efficiency were explored. No further improvement in the preconcentration recovery was obtained upon prolonging the centrifugation time and rate; thus, a centrifugation time of 15 min and a rate of 3500 rpm were selected as the optimal parameters.

According to the experimental data shown in Fig. 2 and 3, the equilibrium temperature, pH, and concentrations of surfactant agents and chelating agents were optimized to obtain the maximum recoveries and reproducibility for Pb, Cd, and Fe based on CPE. Other experimental parameters including equilibrium time, centrifugation time, centrifugation rate, and the final sample volume were also optimized based on average preconcentration recoveries. Table 5 summarizes the optimization of these experimental factors.

Under the optimal conditions, samples containing 0.005 lead(II), 0.005 cadmium(II), and 0.025 ppm iron(III), were successfully separated and preconcentrated using CPE. With detection by FAAS, the maximum recoveries of this method for Pb, Cd, and Fe were 99.8, 97.3, and 99.3% (Table 6), respectively, with an RSD of 2.3–4.9% (n = 5) and an enrichment factor of 20. The original FAAS detection limits for Pb, Cd, and Fe were reduced by 95% from 0.1, 0.1 and 0.5 to 0.005, 0.005, and 0.025 ppm, respectively.

Applications. To demonstrate the feasibility of this method for measuring Pb, Cd, and Fe in water samples collected from municipal water pipelines and dental unit waterlines, the recoveries and reproducibilities of CPE were examined using spiked samples. The spiked samples were prepared by adding Pb, Cd, and Fe stock solutions of different concentrations (initial sample concentrations of 0.005, 0.005, and 0.025 ppm for Pb, Cd, and Fe, respectively) to drinking water and dental water samples. After preconcentration under the optimal experimental parameters, the recoveries and relative standard deviations (RSDs) were obtained and are shown in Table 7. The results demonstrated the capability of this approach for measuring Pb, Cd, and Fe in samples of drinking water and dental water.

TABLE 5. Optimal Experiment Factors and their Corresponding Value

Optimized factors	Iron	Cadmium	Lead
Equilibrium temperature, °C	70	70	70
pH	8.0	10.0	9.0
Concentration of Triton X-114 (mL/100 mL, v/v)	0.2%	0.2%	0.2%
Concentration of DPT (mL/100 mL)	2.5%	2.0%	2.0%
Concentration of NR (mL/100 mL)	0.2%	0.1%	0.2%
Equilibrium time (min)	25	25	25
Centrifuge time (min)	15	15	15
Centrifuge rate (RPM)	3500	3500	3500
Volume of final sample, mL	5	5	5

TABLE 6. Comparison of LOD, MCL, and LOD after Preconcentration and their Maximum Recoveries

Parameter	Lead	Cadmium	Iron
Detection limits of FAAS, ppm	0.1	0.1	0.5
EPA MCL, ppm	0.015	0.005	0.3
FAAS detection limits after preconcentration, ppm	0.005	0.005	0.025
Maximum recovery, %	99.8	97.3	99.3

TABLE 7. Preconcentration Recoveries and RSD of Spiked Real Samples (n = 3)

Sample	Element	Added, µg/L	Found, µg/L	RSD	Recovery, %
Drinking water	Pb	5.0	4.9	1.0	98.6
	Cd	5.0	4.9	3.2	97.3
	Fe	25.0	24.2	2.5	96.8
Dental water	Pb	5.0	5.0	1.5	99.4
	Cd	5.0	4.8	2.8	96.2
	Fe	25.0	24.6	3.0	98.5

Conclusions. Compared with the traditional CPE methods, this new method demonstrated higher recoveries and reproducibility for the detection of multiple metallic trace elements. The liquid-solid phase separation in this approach can be completed using a simple sample pretreatment method that does not require additional accessories such as FIS or multi-walled carbon nanotubes for sample mixing. The experimental results indicated that this new method provides a simple, rapid, and inexpensive approach to the separation, preconcentration, and determination of Pb, Cd, and Fe in water and tap water samples. The potential applications of this method for the detection of metallic trace elements with other instruments, such as ICP-OES and GFAAS, will be investigated shortly.

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