Original Paper

Cloud Point Extraction Preconcentration of Trace Cadmium as 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone Complex and Determination by Flame Atomic Absorption Spectrometry

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Abstract. A new method for the determination of trace cadmium in water samples by flame atomic absorption spectrometry (FAAS) after cloud point extraction (CPE) is proposed. The method is based on the complexation of Cd with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) in the presence of non-ionic micelles of Triton X-100. The effect of experimental conditions such as pH, concentration of chelating agent and surfactant, equilibration temperature and time on cloud point extraction was studied. Under the optimum conditions, the detection limits are 0.64 ng mL\(^{-1}\) with relative standard deviations (RSDs) of 2.1% (n = 10). The proposed method was applied to the determination of trace cadmium in water samples with satisfactory results.

Key words: Cloud point extraction; cadmium; FAAS.

It is now widely accepted that cadmium is among the most dangerous of all metal contaminants in environmental systems. Cadmium can accumulate in living organisms, and its toxic potential is very high. Long-term consumption of drinking water containing cadmium at levels higher than 0.005 mg L\(^{-1}\) can cause nausea, salivation, diarrhea, muscular cramps, renal degradation, lung insufficiency, bone lesions, cancer and hypertension in humans [1, 2]. Its wide technological use (in fertilizers, mining, pigments) and its production from burning oil and coal and incinerating waste bring about extensive anthropogenic contamination of soil, air and water. Consequently, the determination of cadmium concentrations in man-made and natural water resources is of great interest in order to keep a check on the eco-system.

Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions because of the relatively simple and inexpensive equipment required. However, direct determination of metal ions at trace levels by FAAS is limited not only due to insufficient sensitivity, but also by matrix interference. For this reason, preliminary separation and preconcentration of trace elements from the matrix is frequently necessary to improve the detection limit and the selectivity. The most widely used techniques for the separation and preconcentration of trace elements include liquid–liquid extraction [3], co-precipitation [4], ion-exchange [5], solid-phase extraction [6, 7] etc.

Separation and preconcentration based on cloud point extraction (CPE) is becoming an important and practical application of surfactants in analytical chemistry [8, 9]. The technique is based on the
property of most non-ionic surfactants in aqueous solutions to form micelles and become turbid when heated to a temperature known as the cloud point temperature. Above the cloud point, the micellar solution separates into a small volume of surfactant-rich phase and a diluted aqueous phase, in which the surfactant concentration is close to the critical micellar concentration (CMC). Any analyte solubilized in the hydrophobic core of the micelles will separate and become concentrated in the small volume of the surfactant-rich phase.

The use of preconcentration steps based on phase separation by cloud point extraction [10, 11] offers a convenient alternative to more conventional extraction systems. The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, fast, and of lower toxicity to the environment than extractions that use organic solvents. CPE also provides results comparable to those obtained with other separation techniques. Accordingly, any species that interacts with the micellar system, either directly (generally hydrophobic organic compounds) or after a prerequisite derivatization reaction (e.g., metal ions after reaction with a suitable hydrophobic ligand) may be extracted from the initial solution and also be preconcentrated.

Cloud point methodology has been used to separate and preconcentrate organic compounds as a step prior to their determination in hydrodynamic analytical systems such as liquid chromatography [12, 13] and capillary electrophoresis [14]. The phase separation phenomenon has also been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes [15, 16]. U⁶⁺ [17], Er³⁺ [18], and Gd³⁺ [19] have been determined by spectrophotometry, Pd²⁺ [20] by room temperature phosphorescence, Cu²⁺ and Cr³⁺ [21] by ICP-AES, Cu²⁺ [22], Cd²⁺ [23–27], Ag⁺ [28], Ni²⁺ and Zn²⁺ [29], Fe³⁺, Co²⁺ and Ni²⁺ [30], Cr³⁺ and CrO₄⁻[31] by FAAS after CPE using complexing agents.

When cloud point extraction is employed in conjunction with FAAS, the generation of suitable chelating complexes is the main step in the analysis. Several ligands, such as 8-hydroxyquinoline (Oxine) [21, 31], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [18], 1-(2-pyridylazo)-2-naphthol (PAN) [23, 29], 1-(2-thiazolylazo)-2-naphthol (TAN) [24], ammonium pyrrolidinedithiocarbamate (APDC) [30], dialkylthiophosphates (DDTP) [25], and dithizone [28], have been used in cloud point extraction of metal ions. The chelating reagent 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP), which forms complexes with more than 40 metal ions and has found numerous applications in trace element separation and preconcentration by solvent extraction [32–35], has previously not been used in cloud point preconcentration. The aim of this study was to optimize the use of PMBP in cloud point extraction and to assess its application to the preconcentration of cadmium prior to flame atomic absorption spectrometry using Triton X-100 as surfactant. The proposed method was applied to the determination of trace amounts of cadmium in water samples.

**Experimental**

**Apparatus**

A WFX-130 atomic absorption spectrophotometer (Beijing Second Optics, Beijing, P.R. China) equipped with deuterium lamp background correction was used for the determination of Cd in the surfactant-rich phase. A Cd hollow cathode lamp operating at 228.8 nm was used as the radiation source. The lamp current, slit width and observation height was set at 2.5 mA, 0.4 nm and 7 mm, respectively. Other instrumental parameters were adjusted according to the manufacturer’s recommendations. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, P.R. China) supplied with a combined electrode. A thermostated bath maintained at the desired temperatures was used for the cloud point experiments. An 80-2 centrifuge (Changzhou Guohua Electric Appliance Co. Ltd., P.R. China) was used to accelerate the phase separation.

**Reagents and Solutions**

The non-ionic surfactant Triton X-100 was obtained from Amresco (USA) and was used without further purification. Stock standard solution of cadmium at a concentration of 1000 μg mL⁻¹ was obtained from the National Institute of Standards (Beijing, P.R. China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A 1.0 × 10⁻² M solution of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was prepared by dissolving appropriate amounts of this reagent in absolute ethanol from the commercially available product (The First Reagent Factory, Shanghai, China). A stock buffer solution (0.1 M) was prepared by dissolving appropriate amounts of Na₂B₄O₇.10H₂O in doubly distilled water. All other reagents were of analytical reagent grade or better. Doubly distilled water was used throughout the entire study. The pipettes and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with doubly distilled water.

**Cloud Point Extraction Procedure**

For the CPE, aliquots of 10 mL of a solution containing the analytes, Triton X-100 and PMBP buffered at a suitable pH were kept in the thermostatic bath maintained at 80 °C for 25 min. Since the