# Design of rapidly synergistic cloud point extraction of ultra-trace lead combined with flame atomic absorption spectrometry determination

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## ARTICLE INFO

## ABSTRACT

In this work, traditional cloud point extraction (CPE) pattern was changed and improved by the proposed rapidly synergistic CPE. Using octanol as cloud point revulsant and synergic reagent, non-ionic surfactant Triton X-114 (TX-114) accomplished room temperature extraction rapidly without heating in water bath. The improved extraction was named as rapidly synergistic cloud point extraction (RS-CPE). Compared with traditional CPE, RS-CPE was accomplished in 1 min with considerably high extraction efficiency. The improved CPE pattern was coupled with flame atomic absorption spectrometry (FAAS) for the extraction and detection of trace lead in real and certified water samples with satisfactory analytical results. The proposed method greatly improved the sensitivity of FAAS for the determination of lead. Under the optimal conditions, the limit of detection (LOD) for lead was 4.3 μg/L, with enhancement factor (EF) of 39. Factors influencing RS-CPE efficiency, such as concentrations of surfactant TX-114 and octanol, concentration of chelating agent, pH, conditions of phase separation, environmental temperature, salt effect and instrumental conditions, were studied systematically.

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## 1. Introduction

Among kinds of advanced preconcentration methods, cloud point extraction (CPE) has been well developed and applied in many fields of sample pretreatment and analysis in recent decade. Yazdi [1] reviewed the surfactant-based extraction methods recently, which described detailed research works relative to CPE. Besides that, CPE has been well-documented in huge amount of literatures. Many kinds of instrumental methods including flame atomic absorption spectrometry (FAAS) [2,3], thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) [4,5], graphite furnace atomic absorption spectrometry (GF-AAS) [6,7], W-coil ET-AAS [8,9], inductively coupled plasma optical emission spectrometry (ICP-OES) [10,11], inductively coupled plasma mass spectrometry (ICP-MS) [12,13], gas chromatography (GC) [14], high-performance liquid chromatography (HPLC) [15,16], capillary electrophoresis (CE) [17], and chemiluminescence (CL) [18] have been applied to be combined with CPE technique for the determination of metals or organic analytes.

Traditional CPE depended on the heating in water bath to reach or exceed the cloud point temperature (CPT) of the selected surfactant. The solution became turbid with the occurrence of micelle of surfactant and accomplished extraction of target analytes under certain incubation temperature. The extraction procedure was time-and labor-consuming

and no less than 40 min for heating, incubation and cooling was needed [9]. At the early stage of CPE development, kinds of samples to be determined or types of instruments to be coupled with were the main objects of the study. During the later period, many research works were dedicated to improve traditional CPE in many aspects. In order to improve the selectivity of traditional CPE, Wu et al. established displacement-CPE and determined trace silver in complicated matrices [19]. Recently, Gao et al. simplified Wu's displacement-CPE procedure and developed one-step displacement CPE for FAAS determination of trace copper [20]. Although these works improved the analytical performance of traditional CPE in some degree, the extraction patterns still depended on the heating in water bath to realize the cloud point phenomenon. In the aspect of simplifying CPE process, flow injection analysis (FIA) was utilized to realize the on-line coupling of CPE with analytical instruments, such as fixing the heating unit into FIA system [21,3] or excluding the heating treatment by salt-out effect [22,23].

Simplification and improvement of traditional CPE pattern were practical and promising topics. It was reported that octanol and other organic solvents could decrease the CPT of Triton X-100 [24]. However, TX-100 was relatively less used in traditional CPE for its higher CPT (65 °C), which was difficult to make the solution turbid and afford high extraction efficiency. TX-114 was one of the most applied reagents in CPE for its lower CPT (30 °C). In this work, octanol worked as cloud point revulsant of TX-114 and synergic reagent for extraction. Rapid cloud point extraction was realized at the room temperature (about 20 °C) without heating units or adding salts. Thus, traditional CPE pattern was considerably simplified and

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accelerated. Only 1 min was needed for the improved extraction compared with traditional CPE (about 40 min). The proposed extraction method could be named as rapidly synergistic cloud point extraction (RS-CPE).

In this study, FAAS was investigated to be coupled with the proposed RS-CPE for the determination of lead. This metal element is seldom reported to be directly detected by FAAS for its poor sensitivity. Lots of work reported the combination of CPE with FAAS for the determination of metal ions or their species, but almost all the works still depended on heating in water bath to accomplish CPE procedure. Here, RS-CPE was applied to concentrate trace lead thus to improve the sensitivity of FAAS for the determination. RS-CPE conditions and analytical performance were investigated in detail. To the best of our knowledge, there has been no report on application of RS-CPE using TX-114 as surfactant coupled with FAAS for the determination of lead. The surfactant TX-114 based RS-CPE technique was so simple and rapid that only 8 min or so was required for whole extraction and determination process. The sensitivity of FAAS for the determination of lead was considerably improved. Characteristics and performance parameters of the proposed method RS-CPE were described below.

## 2. Experimental

### 2.1. Apparatus

FAAS Model AA-6200 (Shimadzu Instrumental Co., Japan) was used for quantitative analysis of lead.

A centrifuge Model TDL-5-A (Shanghai Anting Scientific Instrument Factory, Shanghai, China) was used to facilitate phase separation.

The pH values were measured by a pH-meter Model pHS-25 (Shanghai Hongyi Instrument Co., Ltd, Shanghai, China).

### 2.2. Reagents

Lead standard stock solution (1000 mg/L) was purchased from National Standard Material Center (Beijing, China). Working standard solutions were obtained daily by stepwise dilution from standard stock solution with Double Distilled Water (DDW). Non-ionic surfactant Triton X-114 (TX-114) (Sigma-Aldrich) and octanol (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used as extractant and cloud point revulsant/synergic reagent, respectively. Dithizone (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was used as the chelating reagent for lead. Other chemical reagents including methanol, ethanol, tetrachloromethane ($CCl_4$), chloroform ($CHCl_3$), acetone and Tetrahydrofuran (THF) were all of analytical grade or better, as well as the reagents mentioned above.

DDW was used throughout the whole work.

### 2.3. Rapidly synergistic cloud point extraction (RS-CPE) procedure

The improved extraction procedure was schematically illustrated in Fig. 1. For each sample, 40 mL analytical solution containing lead and proper amount of chelating agent dithizone were mixed in the solution. After adjusting the pH value, the proper volume of TX-114 and octanol were added into the conical tube. After shaking, the mixture solution became turbid by the effect of octanol. The extraction was accomplished in 1 min under shaking. The complex of Pb–dithizone was captured by the micelle of TX-114 and dispersed octanol. After centrifugation, the turbid solution became pellucid and the micelle rich phase with octanol capturing complex was supernatant in the solution, as the original images shown in Fig. 1. The lower water phase was blotted up carefully and then the proper type of diluting solvent (1 mol/L $HNO_3$ in methanol) was adopted to properly dilute the surfactant-rich phase to 2 mL to decrease viscosity, considering the sampling efficiency of FAAS. After that, the resultant sample was transported to FAAS for determination. The whole process was so simple and rapid that only about 8 min was needed.

### 2.4. Sample collection and preparation

Tap water was collected in our laboratory after flowing for about 5 min, river and lake water were gotten from Xier River and Erhai Lake (Dali, China). All the real water samples above were filtered through a 0.25 μm micropore membrane prior to use. The certified water sample GBW (E) 080393 was directly detected after RS-CPE.

## 3. Results and discussion

### 3.1. Parameters of FAAS instrument

In this work, FAAS was coupled with the advanced RS-CPE preconcentration. Parameters for detection of lead were recommended by instrumental provider and summarized below: absorption line: 283.7 nm, hollow cathode lamp (HCL) current: 10 mA, flow rate of acetylene: 2.0 L/min, flow rate of air: 8.0 L/min, spectral bandwidth: 0.7 nm.
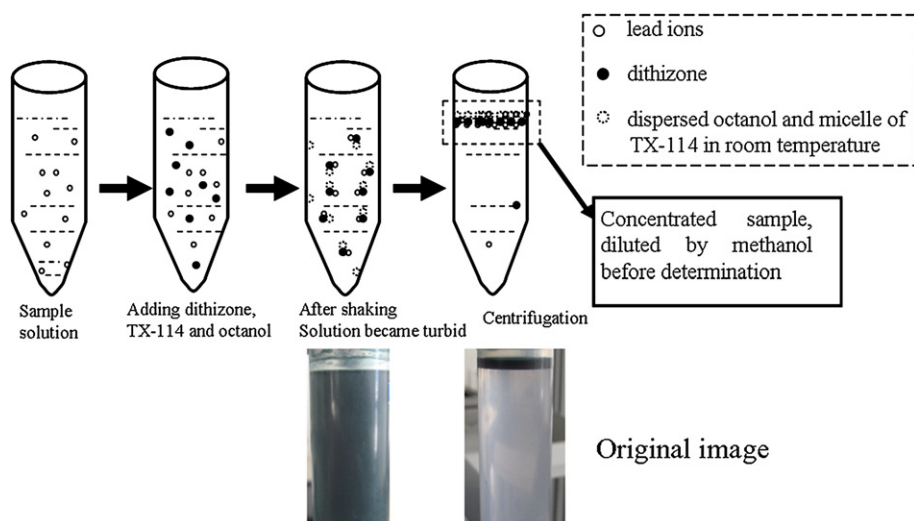


Fig. 1. Schematic diagram of rapidly synergistic cloud point extraction (RS-CPE) procedure.