

# Determination of trace nickel in water samples by cloud point extraction preconcentration coupled with graphite furnace atomic absorption spectrometry

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## Abstract

A new method based on the cloud point extraction (CPE) preconcentration and graphite furnace atomic absorption spectrometry (GFAAS) detection was proposed for the determination of trace nickel in water samples. When the micelle solution temperature is higher than the cloud point of surfactant *p*-octylpolyethyleneglycolphenyether (Triton X-100), the complex of Ni<sup>2+</sup> with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) could enter surfactant-rich phase and be concentrated, then determined by GFAAS. The main factors affecting the cloud point extraction were investigated in detail. An enrichment factor of 27 was obtained for the preconcentration of Ni<sup>2+</sup> with 10 mL solution. Under the optimal conditions, the detection limit of Ni<sup>2+</sup> is 0.12 ng mL<sup>-1</sup> with R.S.D. of 4.3% ( $n = 10$ ,  $c = 100$  ng mL<sup>-1</sup>). The proposed method was applied to determination of trace nickel in water samples with satisfactory results.

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**Keywords:** Cloud point extraction; Graphite furnace atomic absorption spectrometry; Nickel

## 1. Introduction

Nickel is a moderately toxic element compared to other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer [1,2]. Moreover, nickel can cause a disorder known as nickel-eczema [3]. Other studies [4,5] show a disease, characterised as occupational disease, increased in patients who consume food and beverage rich in nickel. Environmental pollution monitoring requires determination of nickel in trace levels in various samples.

The determination of trace nickel in water and environmental samples is difficult due to various factors, particularly low concentration and matrix effects. Although graphite furnace atomic absorption spectrometric (GFAAS) method is a powerful analytical tool for determining trace elements in environmental samples, preconcentration and separation techniques are

still necessary. The widely used techniques for the separation and preconcentration of nickel include liquid–liquid extraction [6], coprecipitation [7], ion-exchange [8], solid-phase extraction [9–12] etc.

Separation and preconcentration based on cloud point extraction (CPE) are becoming an important and practical application of surfactants in analytical chemistry [13,14]. CPE has been used to separate and preconcentrate organic compounds as a step prior to their determination by liquid chromatography [15] and capillary electrophoresis [16]. The phase separation phenomenon has been also used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes [17,18]. CPE as a preconcentration step in conjunction with detection by spectrophotometry, FIA-spectrofluorimetry, FAAS, ICP-AES and HPLC for the determination of various metal ions has been widely studied [19–26]. CPE combination with FAAS for the determination of nickel has also been reported [27–31].

CPE coupled with GFAAS can attain detection limits that are up to 100 times lower compared with respective FAAS configuration [18]. In this paper, a CPE method based on the complex of Ni<sup>2+</sup> with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)

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Table 1  
Operating parameters for GFAAS

Parameters	
Lamp current (mA)	4.0
Wavelength (nm)	232.0
Slit (nm)	0.2
Ar flow rate (mL min <sup>-1</sup> )	200
Sample volume (μL)	10
Temperature program	
Drying	100 °C (ramp 18 s, hold 10 s)
Ashing	800 °C (ramp 10 s, hold 10 s)
Atomizing	2300 °C (ramp 0 s, hold 5 s)
Cleaning	2400 °C (ramp 1 s, hold 3 s)

and using *p*-octylpolyethyleneglycolphenyether (Triton X-100) as surfactant is proposed for the preconcentration of nickel in water samples prior to its determination by GFAAS. The main factors affecting the cloud point extraction were investigated in detail. The proposed method was applied to determination of trace nickel in water samples with satisfactory results.

## 2. Experimental

### 2.1. Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge Genereal Instrument Co. Ltd., Beijing, PR China) with a deuterium background correction and a GF990 graphite furnace atomizer system was used. A nickel hollow-cathode lamp was used as radiation source at 232.0 nm. The optimum operating parameters for GFAAS are given in Table 1. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, PR 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., PR China) was used to accelerate the phase separation.

### 2.2. Reagents and solutions

The non-ionic surfactant Triton X-100 was obtained from Amresco and was used without further purification. Stock standard solution of Ni<sup>2+</sup> at a concentration of 1000 μg mL<sup>-1</sup> was obtained from the National Institute of Standards (Beijing, PR China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. A 1.0 × 10<sup>-2</sup> M solution of PMBP was prepared by dissolving appropriate amounts of this reagent in absolute ethanol from the commercially available product. A buffer solution of 0.1 mol L<sup>-1</sup> NaAc–HAc was used to control the pH of the solutions. 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.

### 2.3. Procedures

For the CPE, aliquots of 10 mL of a solution containing the analyte, 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 surfactant density is 1.07 g mL<sup>-1</sup> therefore, the surfactant-rich phase can settle through the aqueous phase. The phase separation was accelerated by centrifuging for 5 min at 3000 rpm. After cooling in an ice-bath, the surfactant-rich phase became viscous and was retained at the bottom of the tube. The aqueous phases can readily be discarded simply by inverting the tubes. To decrease the viscosity of the extract and to allow its pipetting, 300 μL of a methanol solution containing 0.1 M HNO<sub>3</sub> was added to the surfactant-rich phase. 10 μL samples were introduced into the GFAAS by manual injection. Calibration was performed against aqueous standards submitted to the same cloud point extraction procedure. A blank submitted to the same procedure described above was measured parallel to the samples and calibration solutions.

### 2.4. Analysis of water samples

Prior to the preconcentration procedure, all the water samples were filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and were stored at 4 °C in the dark. To a 10 mL water sample, 1.0 mL of a solution containing 30 g L<sup>-1</sup> Triton X-100 and 1.0 × 10<sup>-2</sup> M PMBP and 1.0 mL of 0.1 M NaAc–HAc buffer solution (pH 5.0) were added. Then the above steps were followed.

## 3. Results and discussion

### 3.1. Effect of pH on CPE

The formation of metal-chelate and its chemical stability is the two important influence factors for CPE. The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE. The effect of pH on the extraction of Ni<sup>2+</sup> complexes was studied and the result shows that extraction was quantitative for nickel in the pH range 3.0–8.0. Hence, a pH of 5.0 was chosen for the subsequent work.

### 3.2. Effect of PMBP concentration

Ten milliliter of a solution containing 1 μg of Ni<sup>2+</sup> in 3.0 g L<sup>-1</sup> Triton X-100 and at a medium buffer of pH 5.0 containing various amounts of PMBP were subjected to the cloud point preconcentration process. The extraction yield increased up to a PMBP concentration of 5 × 10<sup>-4</sup> M and reaches near 100% extraction efficiency. A PMBP concentration of 1.0 × 10<sup>-3</sup> M was chosen to account for other extractable species that might potentially interference with the assaying of Ni<sup>2+</sup>.

### 3.3. Effect of Triton X-100 concentration

A successful CPE would be that maximizes the extraction efficiency through minimizing the phase volume ratio, thus max-

imizing its enrichment factor. The variation in extraction efficiency of nickel within the Triton X-100 range of 0.1–6.0 g L<sup>-1</sup> was examined. Quantitative extraction was observed when the Triton X-100 concentration above 3.0 g L<sup>-1</sup>. So a concentration of 3.0 g L<sup>-1</sup> was chosen as the optimum surfactant concentration in order to achieve the highest possible extraction efficiency.

### 3.4. Effects of equilibration temperature and time

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient separation of phases. The dependence of extraction efficiency upon equilibration temperature and time was studied with a range of 60–120 °C and 5–30 min, respectively. The results showed that an equilibration temperature of 80 °C and a time of 25 min were adequate to achieve quantitative extraction.

### 3.5. Interferences

The effects of common coexisting ions on the extraction of Ni<sup>2+</sup> were tested. The tolerance limits of the coexisting ions were taken as the largest amount making the recovery of Ni<sup>2+</sup> less than 90%. The tolerable concentration ratio of foreign ions to 0.1 µg mL<sup>-1</sup> Ni<sup>2+</sup> was found to be 1000 for K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, 100 for Al<sup>3+</sup> and Ba<sup>2+</sup>, 50 for Cu<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup>, 10 for Cd<sup>2+</sup>, Mn<sup>2+</sup> and Pb<sup>2+</sup>, 5 for Fe<sup>3+</sup> and Cr<sup>3+</sup>, 1000 for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>, 100 for PO<sub>4</sub><sup>3-</sup> and SiO<sub>3</sub><sup>2-</sup>. It can be seen that the major ions in water samples have no obvious influence on CPE of Ni<sup>2+</sup> under the selected conditions.

### 3.6. Characteristics of the method

A calibration curve was constructed by preconcentration 10 mL of sample standard solutions with Triton X-100. Under the optimum experimental conditions, the calibration curve for Ni<sup>2+</sup> is linear up to 300 ng mL<sup>-1</sup> with a correlation coefficient (*r*) of 0.9986. The relative standard deviation (R.S.D.) for 10 replicate determination of 100 ng mL<sup>-1</sup> Ni<sup>2+</sup> is 4.3%. Preconcentration of 10 mL sample gave a detection limit of 0.12 ng mL<sup>-1</sup> (3σ). The enrichment factor, calculated as the ratio of absorbance of preconcentration sample to that obtained without preconcentration, is 27.

There are some publications on cloud point extraction of nickel for atomic spectrometric determination [27–31]. The enrichment factor of our method is similar to those reported in reference 27, 28 and 30, and the detection limit is better than them. Reference [29,31] obtained larger enrichment factor (65 and 74) for nickel, but they used a larger volume of initial solution (50 and 70 mL). It should be mentioned that the enrichment factor of our method could also be improved by using larger volumes of initial solutions.

### 3.7. Analysis of real samples

The accuracy of the proposed method was examined by analyzing Ni in environmental water reference material

Table 2  
Determination of Ni<sup>2+</sup> (ng mL<sup>-1</sup>) in natural water samples (*n* = 5)

Samples	Added	Found	Recovery (%)
Tap water	0	nd	–
	50	53	106
	100	102	102
Lake water	0	8.7	–
	10	18.5	98
	20	29.5	104

nd: no detected.

(ERMs, GSBZ 5009-88, PR China). The analytical value (0.48 ± 0.03 µg mL<sup>-1</sup>) is in good agreement with the certified value (0.50 ± 0.02 µg mL<sup>-1</sup>).

The proposed method has been applied to the determination of Ni<sup>2+</sup> in tap and lake water samples collected in Wuhan, PR China. In addition, the recovery experiments of different amounts of nickel were carried out, and the results were shown in Table 2. The results indicated that the recoveries were reasonable for trace analysis, in a range of 98–106%.

## 4. Conclusions

In this work, the use of micellar systems as a separation and preconcentration for nickel offers several advantages including low cost, safety, preconcentration nickel with high recoveries and very good extraction efficiency. The surfactant-rich phase can be easily introduced into the graphite furnace after dilution with methanol and directly determined by GFAAS. The proposed method can be applied to the determination of trace nickel in various water samples.

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