Simultaneous preconcentration of cobalt, nickel and copper in water samples by cloud point extraction method and their determination by flame atomic absorption spectrometry

Hongbo Xu\textsuperscript{a}, Wanping Zhang\textsuperscript{a}, Xiaoshun Zhang\textsuperscript{b}, Jing Wang\textsuperscript{a}, Jian Wang\textsuperscript{a,*}

\textsuperscript{a}College of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China
\textsuperscript{b}Department of Trace Testing Technology, China Criminal Police College Institute, Shenyang 110854, China

Abstract:

A new cloud point extraction procedure was established for the simultaneous preconcentration and determination of cobalt(II), nickel(II), and copper(II) ions in water samples. After complexation with 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol (5-Br-PADAP), the analytes could be competitively extracted in a surfactant octylphenoxypolyethoxyethanol (TritonX-114), prior to determination by flame atomic absorption spectrometry (FAAS). The effects of pH, the concentrations of chelating agent and surfactant, equilibration temperature and time, sample volume, etc on CPE were studied. The preconcentration factor obtained was 25 and the limits of detection (DL) obtained for cobalt(II), nickel(II), and copper(II) were 2.4, 1.7 and 1.5 ng·mL\textsuperscript{-1}, respectively. Standard reference material of poplar leaf (GBW 07604) was analyzed by the proposed methods, giving results of cobalt(II), nickel(II), and copper(II) found contents in consistency with the standard values. The presented preconcentration procedure was successfully applied to determination cobalt(II), nickel(II), and copper(II) in water samples.

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Keywords: Cloud point extraction; Triton X-114; 2-(5-bromo-2-pyridylazo)-5-(diethylamino) phenol; Cobalt; nickel; copper

1. Introduction

Cobalt, one of the common toxic metals affecting the environment, was present in the waste water of nuclear power plants and many other industries such as electroplating, paints, pigments and electronic [1]. Nickel is the metal component of the enzyme urease and was considered to be essential for plants and some domestic animals. More attention has been paid on the toxicity of nickel in low concentration [2].

*Corresponding author. Tel.: +86-412-5929269; fax: +86-412-5929627.
Email address: anshanxuhb@163.com.
Copper is a nutritionally essential metal and is widely distributed in nature [3]. Therefore, the determination of trace amounts of cobalt, nickel and copper in several matrices samples is very important for some areas, such as environmental chemistry and food control.

Inductively coupled plasma optical emission spectrometry, inductively coupled plasma mass spectrometry, atomic absorption spectrometry, UV-VIS spectrometer, etc. have been used for the determination of the trace metals [4]. In many cases the determination of the trace metals in water samples by FAAS is notably difficult due to the low levels of these metals in the samples and the high complexity of the sample matrices [5]. Thus separation and preconcentration procedures is required for elimination or minimization of matrix effects and concomitants, lowering the detection limit of many metals with different techniques and enhancing the detectability for many metals [6]. In this manner a large number of techniques for the preconcentration of cobalt, nickel and copper, including coprecipitation [7], liquid-liquid extraction [8], microextraction [9], solid phase extraction [10, 11], etc. have been developed.

Cloud point extraction (CPE) method used the water as the solvents, avoided the use of large amounts of the expensive, toxic and flammable organic solvents and is becoming the important and practical applications of the using surfactants in analytical chemistry [12]. When cloud point extraction is employed for the extraction of metal ions, the generation of suitable chelating complexes is the main step in analysis. Several ligands, such as 1-(2-pyridylazo)-2-naphthol (PAN) [13], ammonium pyrrolidine-dithiocarbamate (APDC) [14], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) [15], Dithizone [16], etc. have been used in cloud point extraction of cobalt, nickel and copper ions. In analytical chemistry, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) has also been used as the chelating agent to the sensitive determination of the metals. The metals with 5-Br-PADAP as the chelating agent in the CPE have Cd (II), Pb (II), Hg (II), Cr (III), Co (II), etc. Even so, according our knowledge, the use of 5-Br-PADAP for simultaneous preconcentration of cobalt, nickel and copper has not been reported before.

In this work, a sensitive CPE method for the simultaneous preconcentration and determination of cobalt, nickel and copper ions in water samples using 5-Br-PADAP as sensitized complexing agent and Triton X-114 as surfactant in basic media was established. Several experimental variables affecting the method sensitivity and stability were investigated in detail. The proposed method was applied for the determination levels of metal ions in water samples.

2. Experimental

2.1. Apparatus

A TAS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd., Beijing, PR China) was used in the study. All measurements were carried out in an air-acetylene flame. Cobalt, nickel and copper hollow cathode lamps were used as the radiation source at the wavelengths of 240.7, 232.0 and 324.8 nm, respectively. The operating conditions adjusted in the spectrometer were carried out according to the standard guidelines of the manufacturers. A pHS-25 pH meter (Shanghai Precision and Scientific Instrument Corp., China), an 80-2 centrifuge (Anke Scientific Instrument Factory, China) and a thermostatic bath (Guohua Limited Company, China) were used

2.2. Reagents and solutions

All chemicals used in the experiments were of analytical grade and used without further purification. All solutions were prepared with doubly distilled water. Stock standard solutions at a concentration of 1000 μg·mL⁻¹ were obtained from the National Institute of Standards (Beijing, PR China). Working standard solutions were prepared by appropriate dilution of the stock standard solutions with doubly
2.3. Cloud point extraction procedure

Proposed procedure of cloud point extraction was tested by using model solution. An aliquot of 50mL of a solution containing Co$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ (10-6 μg·mL$^{-1}$), 1mL of 2% (v/v) Triton X-114 and 1 mL of 2×10$^{-3}$ mol·L$^{-1}$ 5-Br-PADAP solution was adjusted to pH 9 with NaOH. The mixture was left to stand in a thermo-stated bath at 50°C for 20 min. Separation of the phases was achieved by centrifugation at 2500 rpm for 10 min. The whole system was cooled in an ice-bath for 10 min in order to increase the viscosity of the surfactant-rich phase. The remaining surfactant-rich phase was dissolved in 2mL of 1.0 mol·L$^{-1}$ HNO$_3$ in ethanol. The concentration of the investigated analyte ions were determined by flame atomic absorption spectrometry in acetylene/air flame. The calibration curves were developed under the optimum conditions of the cloud point extraction procedure.

3. Results and discussion

3.1. Effect of pH on CPE

Since the pH is one of the main parameters for chelation reactions, it was the first variable optimized in the extraction procedure. For that purpose, the effect of pH to the CPE procedure was investigated in the range of 3-10. The effect of pH on the metals recovery is presented in Fig. 1, which shows higher recoveries in the pH range 8-10 for cobalt(II), nickel(II), and copper(II). According to these results, a pH value of 9 was selected for further studies.

![Fig. 1. Effect of pH on the absorbance of analytes.](image)

3.2. Effect of the amount of 5-Br-PADAP

In order to study the influence of the concentration of 5-Br-PADAP on analytical response, the different concentrations of the 5-Br-PADAP were used, and general procedure was applied. The results...
are shown in Fig. 2. The absorbances of the metal ions increased with increasing concentrations of 5-Br-PADAP added and reached a constant value with at least 1 mL of $2 \times 10^{-3}$ mol·L$^{-1}$ 5-Br-PADAP solution. So 1 mL of $2 \times 10^{-3}$ mol·L$^{-1}$ 5-Br-PADAP solution was chosen for the subsequent experiment.

![Graph showing absorbance vs. amount of 5-Br-PADAP](image)

**Fig. 2.** Effect of 5-Br-PADAP concentration on the absorbance of analytes.

### 3.3. Effect of the amount of Triton X-114

The concentration of surfactant that is used in the CPE is a critical factor. Triton X-114 was chosen for the formation of the surfactant-rich phase due to its low cloud point temperature and high density of the surfactant-rich phase, which facilitates phase separation by centrifugation. Thus, amount of Triton X-114 was investigated between 0.5 and 3.0 mL of Triton X-114 (2 %, v/v) for extraction performance. Absorbance values of analyte metal ions were approximately same value in the between 1.0 and 3.0 mL of surfactant. For all the other works, 1.0 mL of 2 % (v/v) Triton X-114 was chosen in order to achieve quantitative extraction and thereby the highest extraction efficiency.

### 3.4. Effects of equilibration temperature and time

In cloud point extraction system, temperature of extraction is a very important parameter for micelles occurring. To achieve easy phase separation, optimal equilibration temperature and incubation time are necessary to complete extraction. The effect of the equilibration temperature and time was studied with a range of 20-70°C and 5-60 min respectively. It was found that an equilibration temperature of 50°C and a time of 20 min were adequate to achieve quantitative extraction.

### 3.5. Effect of sample volume

In order to obtain a high preconcentration factor, the sample volume is one of important analytical factors for preconcentration. Investigated trace metal ions were recovered quantitatively in the all working range (10-50 mL). The preconcentration factor for all ions is calculated by the ratio of the highest sample volume (50 mL) for each analytes and the lowest final volume (2 mL). The preconcentration factor for analytes was calculated as 25.

### 3.6. Characteristics and accuracy of the method

Under the optimum conditions, the calibration graphs were linear in the range of 10-100 μg·L$^{-1}$ cobalt,
nickel and copper. The limit of detection (DL) were 2.4, 1.7 and 1.5 µg·L⁻¹ for cobalt(II), nickel(II), and copper(II), respectively. In order to validate the proposed method, standard reference material of poplar leaf (GBW 07604) was analyzed, giving results of cobalt(II), nickel(II), and copper(II) found contents in consistency with the standard values.

3.7. Determination of cobalt(II), nickel(II), and copper(II) in water samples

The CPE procedure was applied to the determination of Co, Ni and Cu in tap water and river water samples. For this purpose, the samples were filtered to remove the suspended solids and the 50 mL of each of the samples were preconcentrated by proposed method applied which was given in Section 2.3. In addition, recovery experiments for different amounts of Co, Ni and Cu were carried out. The results shown in Table 1 confirm the validity of the proposed method.

Table 1. Determination of analyte ions in water samples using proposed methodology (n=3).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added (µg·L⁻¹)</th>
<th>Found (µg·L⁻¹)</th>
<th>Recovery(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10.1 ± 0.2</td>
<td>101.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.7 ± 0.3</td>
<td>98.5</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9.8 ± 0.2</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.5 ± 0.2</td>
<td>97.5</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>7.5 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>17.1 ± 0.2</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>28.0 ± 0.2</td>
<td>102.5</td>
</tr>
<tr>
<td>River water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9.6 ± 0.2</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20.6 ± 0.2</td>
<td>103.0</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>8.2 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>18.5 ± 0.2</td>
<td>103.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>28.7 ± 0.2</td>
<td>102.5</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>BDL</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>9.9 ± 0.2</td>
<td>99.0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19.5 ± 0.2</td>
<td>97.5</td>
</tr>
</tbody>
</table>

BDL: Below detection limit, mean ± S.D.

4. Conclusion

The cloud point extraction method by using Triton X-114 as surfactant and 5-Br-PADAP as chelating agent was successfully employed for determination of cobalt, nickel, and copper in water samples by FAAS. The method proposed here is simple, rapid, inexpensive, and has good reproducibility. This study
offers a nonpolluting technique for the preconcentration and determination of trace metals.

Acknowledgments

The authors acknowledge the Scientific Research Foundation of Educational Department of Liaoning Province (No. L2012102) and the Administration Foundation of Science and Technology of Anshan City (No. 2011MS13).

References


