Ultrasensitive determination of cobalt and nickel by atomic fluorescence spectrometry using APDC enhanced chemical vapor generation

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A B S T R A C T

Ammonium pyrrolidine dithiocarbamate (APDC) was used to enhance the chemical vapor generation (CVG) efficiency of nickel and cobalt. Volatile nickel and cobalt species were effectively generated through reduction of acidified analyte solution with 2% potassium tetrahydroborate (KBH₄) solution in the presence of 0.02% (m/v) APDC. Thus, a new CVG-atomic fluorescence spectrometric (AFS) method was developed for determination of ultratrace nickel and cobalt. Influencing parameters were evaluated in detail, including the complexing reagents, the concentrations of APDC, nitric acid and KBH₄, flow rates of carrier gas and shield gas, lengths of the reaction tube and the transfer tube, as well as interferences. Under the optimized conditions, the limits of detection (LOD) were 1 ng mL⁻¹ and 6 ng mL⁻¹ for nickel and cobalt, respectively. The calibration curves were linear in the range of 10 to 300 ng mL⁻¹ and 50 to 1200 ng mL⁻¹ for nickel and cobalt, respectively. The potential application of this method was validated by the accurate determination of nickel in three certified reference materials. It was also applied to determination of cobalt in water samples and Vitamin B12 with good recoveries of spiked samples.

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1. Introduction

Chemical vapor generation (CVG) has been widely used in analytical atomic spectrometry because of its obvious advantages of efficient matrix separation, enhanced analyte transport efficiency, efficient analyte atomization, and potential speciation analysis over conventional pneumatic nebulization [1–3]. There are several chemical vapor generation schemes that can be used to convert different analytes into gaseous forms, allowing them to be determined with good sensitivity and selectivity [1,3]. Hydride generation (HG) is the most widely used CVG techniques [4], but the number of elements that can generate hydrides upon derivatization with tetrahydroborate (III) is still limited, which stimulates the development of new CVG systems for more detectable elements. In recent years, CVG has been expanded its scope to transition and noble metals following reaction with tetrahydroborate (III), such as Cu, Fe, Co, Zn, Mn, Au, Ag, Pt, and Pd [5–11]. Recent advances in the CVG of transition and noble metals can be found in some recent comprehensive reviews [12–14].

Trace nickel and cobalt have been the subject of many investigations since they are essential for living organism but toxic when excessive. Therefore, it is important to develop sensitive, rapid, simple and reliable analytical methods to determine ultratrace nickel and cobalt in varied kinds of samples. Conventional nickel CVG procedures involve the reaction of the analyte with carbon monoxide to generate volatile nickel carbonyl species [15–21]. However, the extremely toxic nature of both carbon monoxide and nickel carbonyl largely restricts its wide applications. Volatile nickel and cobalt species were firstly detected by merging acidified sample solution with sodium tetrahydroborate aqueous solution by Wickstrom and co-workers [22]. Very recently, Pohl et al. [23] detected nickel and cobalt volatile species from a HG process although at a very low efficiency. The method was also used to determine nickel in varied samples by chemical vapor generation-inductively coupled plasma optical emission spectrometry (CVG-ICP-OES) [24–26].

As the CVG efficiency of transition and noble metals is much lower compared with conventional hydride-forming elements, great efforts have been made to increase the CVG efficiency of transition and noble metals in recent years. Trace amount of complexing reagents were found to be helpful with improving the CVG efficiency of transition and noble metals, such as sodium diethyl-dithiocarbamate (DDTC) for Au [27–29], 1,10-phenanthroline for Cu [30], Cd and Zn [31], 8-hydroxyquinoline (8-HQ) for Zn and Cd [31]. In this work, we found APDC could remarkably improve the CVG efficiency of nickel and cobalt. An intermittent-flow injection CVG-AFS instrument was used for nickel and cobalt determination due to its low sample and reagent consumption, high sampling frequency, good precision, automated operation, high sensitivity, selectivity and accuracy, and low cost.
This method has been successfully applied to the determination of ultratrace amount of nickel and cobalt in certified reference materials and water samples, respectively.

2. Experimental

2.1. Instrumentation

A Model AFS2202 double-channel non-dispersive atomic fluorescence spectrometer coupled with a programmable intermittent-flow vapor generation apparatus (Beijing Kechuang Haiguang Instrument Co., Beijing, China) was used in this work. High intensity nickel and cobalt hollow cathode lamps (Hebei Ninqiang Instrument Co., Hebei, China) specially designed for AFS were employed as the excitation source, respectively. The schematic diagram of the intermittent-flow vapor generation apparatus was shown in Fig. 1. The flow rate of argon carrier was controlled by a flowmeter in order to operate at low flow rate. A teflon tube was used as a transfer tube and a reaction tube. The operation program of peristaltic pump (Table 1) was controlled by a manufacturer AFS software. A microwave oven (Galanz Co., Guangdong, China) was used to digest the certified reference materials.

2.2. Reagents and materials

The stock standard solutions of Ni and Co (1 mg mL$^{-1}$) were purchased from the National Center for Reference Materials (Beijing, China). Working solutions were freshly prepared daily by appropriate dilution of the stock solutions with distilled deionized water (DDW). The complexing reagent, 0.02% (m/v) ammonium pyrrolidine dithiocarbamate (APDC, Alfa) solution, was obtained by dissolving appropriate amount of APDC with DDW. Other complexing reagents, including ascorbic acid, 8-hydroxyquinoline, dithizone, 5-sulfosalicylic acid, thiourea, 1, 10-phenanthroline, ethylene diamine tetraacetic acid (EDTA) and diethyldithiocarbamate (DDTC), were purchased from Chengdu Kelong Chemical Reagents Co. (Chengdu, China). A solution of 2.0% (m/v) KBH$_4$ was daily prepared by dissolving appropriate amounts of KBH$_4$ (Chengdu Kelong Chemical Reagents Co., Chengdu, China) in 0.5% (m/v) potassium hydroxide solution. Nitric acid, hydrochloric acid, sulfuric acid, potassium hydroxide and hydrogen peroxide were purchased from Chengdu Kelong Chemical Reagents Co. (Chengdu, China). Vitamin B12 injection and tablets were purchased from local market. Certified reference materials, GBW 07605 (tea), GBW 09101b (human hair) and GBW (E) 08608 (simulated water sample) were purchased from National Research Center for CRM (Beijing, China). Tap water was collected in our laboratory, and pond water and river water were obtained from Hehua pond on our campus and Funan River (Chengdu, China), respectively. All samples were stored at 4°C in a refrigerator before analysis.

2.3. Procedure of CVG

As shown in Table 1, in step 1, two sample delivering tubes were put into the sample solution and KBH$_4$ solution, respectively; in step 2, acidic sample solution and KBH$_4$ solution were sucked for 10 s and sample solution was stored in a sample storage coil; then in step 3, the delivering tube for sample solution was changed to the carrier solution; and in the last step (step 4), sample solution was pushed by the carrier into the reaction coil to mix with the KBH$_4$ solution for the CVG reaction. The generated nickel or cobalt volatile species were separated in the gas-liquid separator and swept into the AFS atomizer with the aid of the carrier gas. The AFS atomizer was described in detail in a previous work[32]. Because enough H$_2$ could be produced by the reaction of the acidic sample solution and KBH$_4$ solution, no auxiliary H$_2$ was needed to maintain the Ar/H$_2$ flame. When step 4 is accomplished, the next measurement cycle can be started.

2.4. Sample preparation

Certified reference materials of 0.2047 g tea (GBW 07605) and 0.2326 g human hair (GBW 09101b) were accurately weighed and

<table>
<thead>
<tr>
<th>Step</th>
<th>Flow rate (mL min$^{-1}$)</th>
<th>Time (s)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>6</td>
<td>Put the sampling tube into sample solution</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>Sampling</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>6</td>
<td>Change over the sampling tube into carrier solution</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>16</td>
<td>Readout and clean up</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic diagram of experimental setting. GLS: gas/liquid separator.

Fig. 2. Effect of chelating reagents on the atomic fluorescence intensity of 100 ng mL$^{-1}$ nickel, with concentration of respective chelating reagent of 0.05% (m/v); and “without” means no chelating reagent and 1 mg L$^{-1}$ of Ni.

Fig. 3. Effect of APDC concentration on the atomic fluorescence intensity of 100 ng mL$^{-1}$ nickel and 500 ng mL$^{-1}$ cobalt, respectively.
separately dissolved in 8 mL mixture of nitric acids and hydrogen peroxide ($V_{\text{HNO}_3} : V_{\text{H}_2\text{O}_2} = 6:2$) in closed teflon digestion vessel, and subsequently the samples were digested in a microwave oven with a digestion procedure from a reference method [33], then the digestion solutions were heated near dryness on a hot plate. After cooling, the residue was diluted with 1.5% (m/v) HNO$_3$ and 0.02% (m/v) APDC for the measurement by CVG-AFS. The digestion of Vitamin B12 injection and tablets were also carried out by the same procedure.

3. Results and discussion

3.1. Selection of complexing reagents

Complexing reagents have been used for improving the CVG efficiency of transition and noble metals upon reaction with tetrahydroborate. Xu et al. [30] firstly found that phenanthroline could greatly improve the CVG efficiency of copper. Later, a number of conventionally used complexing reagents were explored as enhancing reagents for the CVG of transition and noble metals [11,27–29,31]. Sun et al. [34] found phenanthroline was able to improve the CVG efficiency of nickel. In this work, we found that APDC gave better performance for nickel CVG than that of phenanthroline. As can be seen from Fig. 2, the nickel CVG efficiency in the presence of APDC was almost twice as that in the presence of phenanthroline. Several other common complexing reagents, including ascorbic acid, EDTA, thiourea and DDTC, were also studied. Generally, the enhancing effects by ascorbic acid and EDTA were minimal; thiourea, DDTC, phenanthroline and APDC could improve the nickel CVG efficiency, and APDC gave the best performance. Thus, APDC was selected for the following investigations and optimal concentration of APDC was found to be 0.02% (m/v), as shown in Fig. 3.

For the cobalt CVG, many complexing reagents such as 8-hydroxyquinoline, dithizone, 5-sulfosalicylic acid, phenanthroline, EDTA, DDTC or APDC were used as an enhancing reagent to improve the CVG efficiency of cobalt. It was found that APDC had optimal signal intensity than other complexing reagents. Therefore, APDC was selected for enhancing reagent for the cobalt CVG. The influence of APDC concentration on the fluorescence intensity of 500 ng mL$^{-1}$ cobalt was studied, with results shown in Fig. 3. Also, the APDC concentration of 0.02% (m/v) was selected for use in this work.

3.2. CVG variables

The CVG generation efficiency highly depended on the reaction acidity and acid types. Preliminary experiments with HCl, HNO$_3$ and H$_2$SO$_4$ showed that HNO$_3$ was the best medium for the CVG. The concentration of HNO$_3$ was studied in the range of 0.5% to 3.0% (v/v) and 1.0% to 4.0% (v/v) for nickel and cobalt, respectively. As can be seen from Fig. 4, the atomic fluorescence intensity of nickel and cobalt were all optimal at the HNO$_3$ concentration of 1.5% (v/v). Meanwhile, the amount of the generated H$_2$ was also enough to maintain the micro Ar/H$_2$ flame. Therefore, 1.5% (v/v) HNO$_3$ was selected for use.

Nickel CVG with tetrahydroborate derivatization eliminates the use of toxic carbon monoxide that is needed in conventional nickel carbonyl generation. A series of KBH$_4$ concentrations in the range of 1.0% to 4.0% (m/v) were studied. As can be seen from Fig. 5, when KBH$_4$ concentration was 2.0% (m/v), the atomic fluorescence intensity of nickel and cobalt were optimal. Excessive amount of hydrogen was produced when KBH$_4$ concentration was higher than 2.0% (m/v), resulting in dramatic dilution and short residence time of volatile
analyte species in the atomizer. Therefore, 2.0% (m/v) KBH₄ was chosen for further experiments.

3.3. AFS instrumental variables

It was reported that the nickel volatile species was highly unstable and fast gas–liquid separation should be a prerequisite to prevent volatile nickel species decomposition [24]. However, at high carrier gas flow rate, the dilution of the volatile species and short residence time of volatile nickel and cobalt species in the atomizer would be dominant, resulting in the decrease of the atomic fluorescence intensity. The effect of Ar flow rate was studied in the range of 50 to 400 mL min⁻¹ and 100 to 400 mL min⁻¹ for nickel and cobalt, respectively, with results shown in Fig. 6. When Ar flow rate was 100 mL min⁻¹ and 150 mL min⁻¹, respectively, the fluorescence intensity of nickel and cobalt was optimal. Argon was also used as shield gas in this work in order to prevent extraneous air from entering the flame, alleviating the interference from the alien environment. The flow rate of the shield gas was evaluated in the range of 500 to 1200 mL min⁻¹ for nickel and cobalt. It was found that 900 mL min⁻¹ argon flow rate was the best.

The length of the reaction tube had a key influence on the atomic fluorescence intensity of nickel and cobalt, as it was a compromise between sample amount and fast gas–liquid separation. The length of the reaction tube was studied in the range of 8 to 18 cm and 11 cm to 21 cm for nickel and cobalt, respectively (Fig. 7), and 12 cm for nickel and 15 cm for cobalt was found to be optimal. The length of the transferring tube between the gas–liquid separator and the AFS torch was also carefully studied. Guo et al. [24] pointed out that nickel volatile species may be decomposed during transportation and the resultant Ni atoms might be adsorbed on the active sites of inner wall surface of the transferring tube, thus the length of the transferring tube should be kept as short as possible. However, in this work, we found that if the transferring tube was too short, the Ar/H₂ micro flame would be unstable. The length of transferring tube was studied in the range of 3 to 13 cm and 5 to 15 cm for nickel and cobalt, respectively. As can be seen from Fig. 8, the fluorescence intensity of nickel and cobalt was found to be the optimal at 7 cm and 9 cm, respectively.

3.4. Evaluation of interference

In this work, several metal and metalloid ions were selected for evaluation of the selectivity of the proposed method, namely Ca(II), Mg(II), K(I), Na(I), Zn(II), Mn(II), Cu(II), Au(I), Ag(I), Cr(III), Bi(III), Pb(II), Cd(II), Ge(IV), Sn(II), Fe(III), Sb(III), As(III), Co(II), Ni(II), Se(IV) and Te(VI). As can be seen from Table 2, macro constituents of Ca(II), Mg(II), K(I), Na(I), Zn(II) and Mn(II) had no significant influence on nickel and cobalt determination. Some transition metal ions and traditional hydride generation elements at high concentrations may still affect the nickel and cobalt CVG.

3.5. Analytical figures of merit and sample analysis

Under the optimal experimental conditions, analytical figures of merit of the proposed method for the determination of nickel and cobalt were established. The calibration curve was linear in the range of 10 to 300 ng mL⁻¹ for nickel (R² > 0.994) and 50 to 500 ng mL⁻¹ for cobalt (R² > 0.998), respectively. The limit of detection (LOD) of 1 ng mL⁻¹ and 6 ng mL⁻¹ for nickel and cobalt was obtained, respectively, on the basis of 3σ criterion for 11 measurements of a blank. The LOD was equivalent to those by similar techniques [24,25]. The relative standard deviation (RSD) calculated from five measurements for nickel at 100 ng mL⁻¹ and cobalt at 500 ng mL⁻¹ was 4.7% and 4.2%, respectively.

To validate the potential application of the proposed method, two biological certified reference samples (GBW 07605 tea and GBW 09101b human hair) and one certified reference water sample (GBW (E) 08608) were analyzed for nickel. The analytical results

<table>
<thead>
<tr>
<th>Sample Added (ng mL⁻¹)</th>
<th>Found (ng mL⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water 0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>- 100</td>
<td>102 ± 10</td>
<td>102</td>
</tr>
<tr>
<td>- 200</td>
<td>196 ± 12</td>
<td>98</td>
</tr>
<tr>
<td>Tap water 0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>- 100</td>
<td>112 ± 15</td>
<td>112</td>
</tr>
<tr>
<td>- 200</td>
<td>216 ± 20</td>
<td>108</td>
</tr>
<tr>
<td>Pond water 0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>- 100</td>
<td>93 ± 10</td>
<td>93</td>
</tr>
<tr>
<td>- 200</td>
<td>190 ± 18</td>
<td>95</td>
</tr>
</tbody>
</table>
were in good agreement with the certified values (Table 3). Three water samples were collected and subjected to cobalt analysis by
the proposed method. The analytical results were shown in Table 4. Good spike-recoveries were in the range of 93–112%. Vitamin B12 injection and tablets were also analyzed for cobalt. The analytical results were in good agreement with the determined values by inductively coupled plasma mass spectrometry (ICP-MS) (Table 5).

4. Conclusion
It has been demonstrated that APDC can greatly improve the generation efficiency of nickel and cobalt volatile species upon tetrahydroborate derivatization. A new CVG-AFS method for ultratrace cobalt analysis by at minimum sacrifice can be easily realized by using this two channel AFS instrument ease of use and low cost. With compromised experimental conditions for CVG of nickel and cobalt elements, their simultaneous determination can be easily realized by using this two channel AFS instrument at minimum sacrifice of sensitivity.

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