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Synergetic enhancement effect of ionic liquid and diethyldithiocarbamate on the chemical vapor generation of nickel for its atomic fluorescence spectrometric determination in biological samples

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ABSTRACT

Room-temperature ionic liquid in combination with sodium diethyldithiocarbamate (DDTC) was used to synergetically improve the chemical vapor generation (CVG) of nickel. Volatile species of nickel were effectively generated through reduction of acidified analyte solution with KBH_4 in the presence of 0.02% DDTC and 25 mmol L^{-1} 1-butyl-3-methylimidazolium bromide ($[C_4mim]Br$) at room temperature. Thus, a new flow injection (FI)-CVG-atomic fluorescence spectrometric (FI-CVG-AFS) method was developed for determination of nickel with a detection limit of 0.65 $\mu g\,L^{-1}$ (3 s) and a sampling frequency of 180 h^{-1}. With consumption of 0.5 mL sample solution, an enhancement factor of 2400 was obtained. The precision (RSD) for eleven replicate determinations of 20 $\mu g\,L^{-1}$ Ni was 3.4%. The developed FI-CVG-AFS method was successfully applied to determination of trace Ni in several certified biological reference materials.

1. Introduction

Chemical vapor generation (CVG) techniques have gained great success in analytical atomic spectrometry because they offer significant benefits as a method of sample introduction, including efficient matrix separation and high analyte transport efficiency as compared with conventional pneumatic nebulisation [1]. However, the number of elements that can generate volatile species upon derivatization with tetrahydroborate(III) is still limited, which stimulates the development of new CVG systems for more elements. In recent years, CVG technique has 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 [2–15]. Recent advances in the CVG of transition and noble metals can be found in two recent excellent reviews [16,17].

In the specific case of Ni, early CVG procedures involve the reaction of the analyte with carbon monoxide to generate volatile nickel carbonyl species [18–23]. However, the extremely toxic nature of both carbon monoxide and nickel carbonyl largely restricts its wide applications. In 2000, Guo et al. [24] reported the generation of volatile nickel species from the acidic mixture of nickel ion and tetrahydroborate(III) for the first time, which avoided the use of carbon monoxide and opened a new door for the CVG of Ni. Later, Marrero and Smichowski [25] made a detailed investigation of the vapor generation conditions for Ni in acidic solution with tetrahydroborate(III) as the reductant with ICP-OES. Cerutti et al. [26] introduced an on-line preconcentration scheme for Ni using activated carbon prior to CVG for ICP-OES detection. Very recently, Sun and Suo [27] reported the determination of the ultra-trace amounts of Ni in environmental samples by CVG with in situ trapping in an iridium–palladium coated graphite furnace.

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 the past few years. Several reagents have been found to improve the CVG of transition and noble metals, such as sodium diethyldithiocarbamate (DDTC) for Au [4,11,28,29], Triton X-100 for Ag [30], cetyltrimethylammonium bromide (CTAB) for Zn [8], 1,10-phenanthroline for Cu [31], Ni [27], Cd and Zn [9], 8-hydroxyquinoline (8-HQ) for Zn and Cd [9], and Ni [27], thiourea, cobalt ion and ascorbic acid for Cd [32,33]. Very recently, we found that some room-temperature ionic liquids (RTILs) were able to improve the CVG efficiency of Cu, Ag and Au [34,35]. To date, only one report has been published on the enhancement effects of reagents on the CVG of Ni [27].

Herein, we report the synergetic enhancement effect of 1-butyl-3-methylimidazolium bromide ($[C_4mim]Br$) and DDTC on the CVG of Ni in acidic aqueous solution with tetrahydroborate(III) as the reductant. As flow injection (FI)-CVG-atomic fluorescence

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spectrometry (FI-CVG-AFS) possesses the advantages of low consumption in sample and reagent, high sampling frequency, good precision, enhanced selectivity, automated operation, high sensitivity, accuracy, and low cost, such enhancement effect was applied to develop a new FI-CVG-AFS method for the determination of trace nickel in biological samples.

2. Experimental

2.1. Instrumentation

A model XGY-1011A nondispersive atomic fluorescence spectrometer (Institute of Geophysical and Geochemical Exploration, Langfang, China) was employed throughout. High-intensity hollow cathode lamp of Ni (Ningqiang Light Sources, Hengshui, China) was used as radiation source. The generated analyte vapor and hydrogen evolved from the reactor were swept into a quartz tube atomizer with an argon flow. The argon flow was controlled by a rotameter. At the outlet of the furnace, the gas mixture was self-ignited, and a hydrogen–argon–air entrained flame was maintained without the addition of any auxiliary hydrogen.

A model FIA-3110 FI system (Titan Instruments Co., Ltd., Beijing, China) was used to deliver acidified sample and borohydride solutions to a home-made gas–liquid phase separator (GLS) [36]. The FIA-3110 consists of two peristaltic pumps and a standard rotary injection valve (8-channel 16-port multifunctional injector). Tygon peristaltic pump tubings were employed to propel the sample and reagent solution. PTFE tubing with 0.5 mm i.d. was used for all connections. These connections were kept as short as possible to minimize the dead volume.

All samples were digested in sealed PFA (Teflon-perfluoralkoxy) vessels on a Model Qwave-2000 microwave digestion system (Questron Co., Canada).

2.2. Reagents

All of the reagents employed were at least of analytical grade. Doubly deionized water (DDW, 18.2 MΩ cm) obtained from a WaterPro water purification system (Labconco Corporation, Kansas City, MO, USA) was used throughout. KBH_4 solution was prepared daily by dissolving KBH_4 (Guangfu Fine Chemical Research Institute, Tianjin, China) in 0.05 mol L^{-1} KOH (Guangfu Fine Chemical Research Institute, Tianjin, China). 0.80 mol L^{-1} HCl solution was used as the carrier solution and also as the medium for subsequent CVG. Stock solution of 1000 mg L^{-1} Ni^{2+} was obtained from the National Research Center for Standard Materials (NRCSM, Beijing, China). Working solutions of Ni^{2+} were prepared by stepwise dilution of the stock solution with DDW (in final dilution appropriate amounts of 2.0 mol L^{-1} HCl were added to make a final solution of 0.16 mol L^{-1} HCl). [C_4mim]Br solution was prepared by dissolving 10 mmol [C_4mim]Br (>97%, Chemer Chemical Co., Hangzhou, China) in 100 mL DDW. DDTC solution was prepared by dissolving 0.05 g of DDTC (Tianjin Institute of Chemicals, Tianjin, China) in 100 mL DDW.

2.3. Procedures

Details on the FI manifold and CVG system used for the FI-CVG-AFS can be found in our previous work [34]. A complete cycle for the determination consists of two steps. In step 1 the injector valve was in the fill position, so that the sample loop (0.500 mL) was filled with the sample solution. In step 2 the injector valve turned to the inject position, so that a carrier solution of 0.80 mol L^{-1} HCl was introduced at a flow rate of 3.8 mL min^{-1} to push the sample solution in the sample loop into the mixing/reaction tube. Meanwhile, the KBH_4 solution was introduced at a flow rate of 3.8 mL min^{-1} for 15 s to react with the analyte in the mixing/reaction tube. The generated volatile species were separated from the liquid phase in the GLS, and delivered into the AFS system with an argon flow for detection. The operating conditions of the instrument are summarized in Table 1.

Table 1
Recommended operating conditions.

Parameter	Settings
Atomic fluorescence spectrometry	
Hollow cathode lamp current (mA)	70
High voltage of PMT (V)	300
Quartz furnace temperature (°C)	200
Read mode	Peak area
Chemical vapor generation	
Sample acidity (HCl) (mol L^{-1})	0.16
Concentration of KBH_4 (g L^{-1})	10
Concentration of [C_4mim]Br (mmol L^{-1})	25
Concentration of DDTC (%, m/v)	0.020
Carrier solution (HCl) (mol L^{-1})	0.80
Carrier gas (argon) flow rate (mL min^{-1})	450
Injection volume (mL)	0.500

2.4. Sample preparation

The following certified biological reference materials (NRCSM, Beijing, China) were employed to validate the proposed method: GBW 10016 (tea), GBW 09101 (human hair), GBW 08513 (tea leaf) and GBW 08571 (mussel). For sample preparation, 0.5 g of the sample was accurately weighed, mixed with 5.0 mL of concentrated HNO_3 and 3.0 mL of 30% H_2O_2, and digested according to the following temperature program: 130 °C for 3 min, 175 °C for 2.5 min, and 180 °C for 4.5 min. After cooling, the digests were transferred to a 100-mL glass beaker, and gently heated on a hot plate to near dryness. The residues were transferred into a 25-mL volumetric flask, appropriate amounts of 2.0 mol L^{-1} HCl were added and the solution was made up to volume with DDW, so that the final sample acidity was 0.16 mol L^{-1} HCl.

3. Results and discussion

3.1. Enhancement effect of [C_4mim]Br and DDTC on the CVG of Ni

The ever reported methods for improving CVG efficiency of transition and noble metals can be principally categorized into three groups: the first is to introduce complexing agents for metal ions to provide more efficient CVG precursors, such as DDTC [4,11,28,29] and 8-HQ [9,27]; the second is to use the surfactants like Triton X-100 [30] and CTAB [8] to modify the reaction medium and to provide micro-environment for stabilizing the resultant volatile species; the third is to employ small molecular compounds or metal ions [32,33] to influence the CVG reaction process. We previously explored RTILs to improve the CVG efficiency of Au, Ag and Cu [34], and suggested that the role of RTILs was to provide more effective CVG precursor, and to afford protective micro-environment [35].

In the present work, the effects of individual DDTC or [C_4mim]Br, or their combination on the CVG of Ni were investigated in detail. [C_4mim]Br was used due to its easy availability and good performance for the CVG of Au [35]. Fig. 1 shows the effect of the concentration of [C_4mim]Br on the CVG-AFS response of Ni in the presence or absence of DDTC (0.020%, m/v). The CVG-AFS response of 20 μg L^{-1} Ni^{2+} significantly increased as the concentration of [C_4mim]Br increased from 0 to 25 mmol L^{-1} in the presence of DDTC (0.020%, m/v). Further increasing the concentration of [C_4mim]Br deteriorated the analytical precision due to excessive foam formation. Optimal concentration of [C_4mim]Br was thus