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Effects of room-temperature ionic liquids on the chemical vapor generation of gold: Mechanism and analytical application

Chuan Zhang, Yan Li, Peng Wu, Yan Jiang, Qian Liu, Xiu-Ping Yan*

Research Center for Analytical Sciences, College of Chemistry, Nankai University, 94 Weijin Road, Tianjin 300071, China

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ABSTRACT

To get insight into the mechanism of the effect of room-temperature ionic liquids (RTILs) on the chemical vapor generation (CVG) of noble metals, gold was taken as a model element, and eight RTILs were examined. All the RTILs resulted in 3–24 times improvement in sensitivity for Au, depending on their nature. For the RTILs with identical anion, the RTILs with the cations of short chain exhibited better enhancement effect than those with long alkyl chain length or complex branch chain. For the RTILs with identical cation, the RTILs with Br^- gave the best enhancement effect. The formation of ion pairs between the cation of RTILs and the anion species of gold via electrostatic interaction, and/or the substitution of the Cl^- in the anion species of gold by the anion of RTILs likely enabled a more effective CVG reaction to occur. The RTILs also facilitated the generation of small bubbles and provided an electrostatic stabilization to protect the unstable volatile gold species and to help fast isolation of volatile gold species from the reaction mixture. 1-Butyl-3-methylimidazolium tetrafluoroborate [C_4mim]Br gave the best improvement in the sensitivity (24 times) among the RTILs studied, and also reduced the interferences from common transition and other noble metals. Based on the enhancement effect of [C_4mim]Br, a novel flow injection–CVG–atomic fluorescence spectrometric method with a detection limit (3*s*) of 1.9 $\mu g\,L^{-1}$ and a precision of 3.1% (50 $\mu g\,L^{-1}$, RSD, $n = 11$) was developed for the determination of trace gold in geological samples.

1. Introduction

Chemical vapor generation (CVG) is a widely used technique for sample introduction into atomization cells in analytical atomic spectrometry due to its improved analyte transport efficiency, elimination/alleviation of the sample matrix effects, and potentiality of speciation analysis [1–3]. In the past decade, great efforts have been made in expanding the CVG to the generation of volatile species of transition and noble metals upon reaction with tetrahydroborate(III) [4–13], although traditional CVG is limited to classic hydride-forming elements such as As, Sb, Se, Sn, Ge, Bi, In, Pb, and Te which are capable of forming stable covalent hydrides. However, the generation efficiency of the volatile species of transition and noble metals is much lower than that of hydride-forming elements, which largely inhibit the practical applications of CVG for transition and noble metals. Several attempts have been made to improve the CVG efficiency for transition and noble metals. For example, the addition of chelating agents has been found favorable for the CVG of Au and Cu [11,12,14,15]. 1,10-Phenanthroline, 8-hydroxyquinoline, thiourea, cobalt ion and ascorbic acid have been used to improve the CVG of Cd and Zn [16,17]. Recently, surfactants have been also employed for stabilizing the volatile species of Ag and Zn [18,19].

Room-temperature ionic liquids (RTILs), as novel solvents, have many fascinating properties which make them of fundamental interest to all chemists. Analytical applications of RTILs are also intrigued regarding that they can be easily handled and used in wide variety of environments [20,21]. Up to now, RTILs have been successfully used as separation media for chromatography and capillary electrophoresis, solvents for extractions, sensing materials for chemosensing, matrixes for MALDI-MS, electrolytes for electrochemistry and also as solvents for analytical spectroscopy such as near infrared spectroscopy, fluorescence spectrometry and Raman spectroscopy [20–26]. Recently, the RTIL of *n*-butylpyridinium tetrafluoroborate ([C_4Py][BF_4]) has been found not only to improve the CVG efficiency of Au, Ag and Cu, but also reduce interferences from common transition metal ions [27]. Despite this, very little is known about the mechanism of the enhancement effect of the RTILs on the CVG of transition and noble metals, which intrigues us to further study the role of RTILs in CVG reaction.

This work was undertaken to make a mechanistic study on the effects of RTILs on the CVG reaction taking Au as a model element. Atomic fluorescence spectrometry (AFS) coupled with a flow injection (FI) technique was selected as the technique of choice for detecting the signal of Au because of the advantages of low consumption in sample and reagent, high sampling frequency, good

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* Corresponding author. Tel.: +86 22 23504605; fax: +86 22 23506075.
E-mail addresses: xpyan@nankai.edu.cn, xiupingyan@gmail.com, xpyan308@yahoo.com.cn (X.-P. Yan).

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precision, enhanced selectivity, automated operation, high sensitivity, accuracy, and low cost [16]. To get insight into the mechanism of the effect of RTILs on the CVG of Au, RTILs with various anions and cations were examined, and UV–vis spectrophotometry was used to elucidate the interactions of RTILs and the analyte. Analytical performance based on the CVG of Au in the presence of RTILs for FI–CVG–AFS determination was also evaluated.

2. Experimental

2.1. Instrumentation

The instrumental set-up for FI–CVG–AFS is similar to that in our previous work [27]. Briefly, a Model FIA-3110 FI system (Titan Instruments Co. Ltd, Beijing, China) was on-line coupled with a nondispersive atomic fluorescence spectrometer (Model XGY-1011A, Institute of Geophysical and Geochemical Exploration, Langfang, China) for the investigation of the CVG of Au. Sample and reductant were mixed with the FI system and then delivered to a home-made gas–liquid phase separator (GLS) for gas–liquid separation. The resultant volatile gold species was then further delivered to the atomic fluorescence spectrometer for detection with the aid of carrier gas. A Shimadzu UV-3600 UV–vis spectrophotometer was used to measure the absorption spectra for investigating the interactions of the RTILs and the analyte.

2.2. Reagents

All of the reagents employed were at least of analytical grade. Deionized distilled 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 fresh 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). Dilute HCl solution was used as the carrier solution and also as the medium for subsequent CVG. Stock solution of 1000 mg L^{-1} Au(III) was obtained from the National Research Center for Standard Materials (NRCSM, Beijing, China). Working solutions of Au(III) were prepared by stepwise dilution of the stock solution. The RTILs of *n*-butylpyridinium tetrafluoroborate $[C_4Py][BF_4]$, *n*-butylpyridinium bromide $[C_4Py]Br$ and 1-hexadecyl-3-methylimidazolium chloride $[C_{16}mim]Cl$ were obtained from Chemer Chemical Co. Ltd. (>97%, Hangzhou, China). Tetrabutyl-ammonium bromide $[N_{4444}]Br$ was purchased from Guangfu Fine Chemical Research Institute (99%, Tianjin, China). 1-Butyl-3-methylimidazolium bromide $[C_4mim]Br$, 1-ethyl-3-methylimidazolium bromide $[C_2mim]Br$, 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4mim][BF_4]$ and tetrabutyl-ammonium tetrafluoroborate $[N_{4444}][BF_4]$ were prepared and purified according to literature [28–31]. Cetyltrimethylammonium bromide (CTAB) and *n*-octyl alcohol (Guangfu Fine Chemical Research Institute, Tianjin, China), and Triton X-114 (Sigma–Aldrich Chemicals Ltd., USA) were also used for a comparative study.

2.3. Procedures

The FI manifold used for the FI–CVG–AFS was adopted from our previous work [27]. The complete cycle of the determination consists of two steps. In step 1 the injector valve was in the fill position, so that the sample loop (500 μL) was filled with the sample solution. In step 2 the injector valve turned to the inject position, so that a carrier acid solution 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)	400
Read mode	Peak area
Chemical vapor generation	
Sample acidity (HCl) (mol L^{-1})	0.6
Concentration of KBH_4 (g L^{-1})	22
Concentration of $[C_4mim]Br$ (mmol L^{-1})	15
Carrier gas (argon) flow rate (mL min^{-1})	450
Injection volume (mL)	0.5

2.4. Sample preparation

The following certified geological reference materials (NRCSM, Beijing, China) were employed to validate the developed FI–CVG–AFS method based on the enhancement of RTILs: GBW 07299 (gold ore) and GBW 07300 (gold ore).

For the determination of Au, 10.0 g of ore sample was accurately weighed in a 10-mL porcelain crucible and heated to 650 °C in a muffle furnace for 4 h. After cooling, the sample was transferred to a 250-mL glass beaker, then 80 mL aqua regia was added. The mixture was heated in a water-bath at boiling temperature for 1 h to dissolve the gold, then transferred to a 100-mL volumetric flask and made up to volume with DDW. The solution required for the final determination was made to contain 0.6 mol L^{-1} HCl.

3. Results and discussion

3.1. Effect of the concentration of RTILs on the CVG of Au

To elucidate the role of RTILs in the CVG of Au, here we investigated the effects of eight RTILs with different anions or/and cations on the CVG of Au. The RTILs involved include $[C_4Py][BF_4]$, $[C_4Py]Br$, $[C_{16}mim]Cl$, $[N_{4444}]Br$, $[C_4mim]Br$, $[C_2mim]Br$, $[C_4mim][BF_4]$ and $[N_{4444}][BF_4]$. Although $[C_4Py][BF_4]$ had been used to improve the CVG efficiency of Au, Ag and Cu in our previous work [27], it was also included here just for a comparative purpose. The structures of these RTILs examined are illustrated in Fig. 1. The effect of the concentration of RTILs on the response of Au is shown in Fig. 2.

The RTILs involved in this study can be categorized into two groups: one with the cations containing short alkyl chain and the other with the cations containing relatively long alkyl chain or more branched chains. All the RTILs tested resulted in an improvement in sensitivity for Au detection to some extent, depending on the nature of RTILs. $[C_4mim]Br$, $[C_4mim][BF_4]$, $[C_2mim]Br$, $[C_4Py][BF_4]$ and $[C_4Py]Br$, belonging to the first group, were studied in the range of 0–24 mmol L^{-1}. The response for Au in the presence of the RTILs in the first group was markedly improved and the maximum improvement (24 times) in sensitivity was obtained with $[C_4mim]Br$ (Fig. 2a). As for the second group, $[N_{4444}][BF_4]$, $[N_{4444}]Br$ and $[C_{16}mim]Cl$ were investigated in the concentration range from 0 to 0.3 mmol L^{-1}. Higher concentrations were not tested as bigger bubbles and serious foams were generated at concentrations above 0.3 mmol L^{-1}, which largely obstructed the CVG reaction. Group 2 RTILs gave only three times enhancement in sensitivity (Fig. 2b). The effects of RTILs depended not only on the cations,