



# Efficient generation of volatile cadmium species using Ti(III) and Ti(IV) and application to determination of cadmium by cold vapor generation inductively coupled plasma mass spectrometry (CVG-ICP-MS)☆



Zikri Arslan <sup>a,\*</sup>, Vedat Yilmaz <sup>a,b</sup>, LaKeysha Rose <sup>a</sup>

<sup>a</sup> Jackson State University, Department of Chemistry and Biochemistry, Jackson, MS 39217, USA

<sup>b</sup> Erciyes University, Faculty of Pharmacy, Department of Analytical Chemistry, 38039 Kayseri, Turkey

## ARTICLE INFO

### Article history:

Received 4 June 2015

Received in revised form 10 June 2015

Accepted 20 June 2015

Available online 26 June 2015

### Keywords:

Cadmium

Chemical vapor generation

Titanium (III)

Titanium (IV)

Inductively coupled plasma mass spectrometry

## ABSTRACT

In this study, a highly efficient chemical vapor generation (CVG) approach is reported for determination of cadmium (Cd). Titanium (III) and titanium (IV) were investigated for the first time as catalytic additives along with thiourea, L-cysteine and potassium cyanide (KCN) for generation of volatile Cd species. Both Ti(III) and Ti(IV) provided the highest enhancement with KCN. The improvement with thiourea was marginal (ca. 2-fold), while L-cysteine enhanced signal slightly only with Ti(III) in H<sub>2</sub>SO<sub>4</sub>. Optimum CVG conditions were 4% (v/v) HCl + 0.03 M Ti(III) + 0.16 M KCN and 2% (v/v) HNO<sub>3</sub> + 0.03 M Ti(IV) + 0.16 M KCN with a 3% (m/v) NaBH<sub>4</sub> solution. The sensitivity was improved about 40-fold with Ti(III) and 35-fold with Ti(IV). A limit of detection (LOD) of 3.2 ng L<sup>-1</sup> was achieved with Ti(III) by CVG-ICP-MS. The LOD with Ti(IV) was 6.4 ng L<sup>-1</sup> which was limited by the blank signals in Ti(IV) solution. Experimental evidence indicated that Ti(III) and Ti(IV) enhanced Cd vapor generation catalytically; for best efficiency mixing prior to reaction with NaBH<sub>4</sub> was critical. The method was highly robust against the effects of transition metal ions. No significant suppression was observed in the presence of Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II) up to 1.0 μg mL<sup>-1</sup>. Among the hydride forming elements, no interference was observed from As(III) and Se(IV) at 0.5 μg mL<sup>-1</sup> level. The depressive effects from Pb(II) and Sb(III) were not significant at 0.1 μg mL<sup>-1</sup> while those from Bi(III) and Sn(II) were marginal. The procedures were validated with determination of Cd by CVG-ICP-MS in a number certified reference materials, including Nearshore seawater (CASS-4), Bone ash (SRM 1400), Dogfish liver (DOLT-4), Mussel tissue (SRM 2976) and Domestic Sludge (SRM 2781).

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## 1. Introduction

Chemical vapor generation (CVG) is an indispensable tool for determination of hydride and vapor forming elements owing its high sensitivity and capability for chemical speciation [1–4]. It has also been an attractive research area for cadmium (Cd) over the two decades in pursuit of more efficient generation of volatile cadmium (Cd) species to develop sensitive detection methods for this highly toxic heavy metal [1–17]. Cacho et al. [5] and D'Ulivo and Chen [6] were the first reporting successful generation of volatile Cd species for analytical purposes. The former generated volatile Cd species in non-aqueous media by using diethyldithiocarbamate (DDTC) in acidic *N,N*-dimethylformamide (DMF) and sodium borohydride (NaBH<sub>4</sub>), whereas the latter used aqueous solution with sodium tetraethylborate (NaBEt<sub>4</sub>).

Since the pioneering reports, it has been realized that the generation of volatile Cd species is an overwhelmingly difficult task due to severe chemical interferences besides poor yield and instability of volatile Cd species [1–15]. In many studies, Au(III), Bi(III), Cu(II), Ni(II), Pb(II), and Zn(II) induced severe suppression whose magnitude varied considerably with the experimental conditions [7,11,14]. Various chelating/masking reagents, including thiourea [11,18–21], L-cysteine [15,21], 8-hydroxyquinoline (8-HQ) [22], 1,10-phenanthroline [22], and potassium cyanide (KCN) [23–26] have been utilized to overcome the depressive effects. Separation procedures based on ion-exchange [27–29], coprecipitation [11] and cloud point extraction [30] have also been employed to separate Cd(II) from interfering elements. Thiourea perhaps has been the most popular of the masking agents as it enhanced Cd vapor generation efficiency in the presence of Co(II) or Ni(II) [11,18–21]. Often the enhancement was modest as high as 5- to 6-fold; yet, thiourea, neither with Co(II) nor with Ni(II), was able to fully alleviate the effects of Cu(II), Pb(II) and Ni(II) [11,18]. Chuachud and Tyson found that thiourea performed better than L-cysteine with Co(II) in HNO<sub>3</sub> medium, but severe interferences were observed from Cu(II) and Fe(III) while others like Se(IV), Sn(II), As(III) and Pb(II) did also depress Cd signals [15,21].

☆ Presented at the 2015 PITTCON Conference & Expo, New Orleans, LA, USA, March 8–12, 2015

\* Corresponding author. Tel.: +1 601 979 2072; fax: +1 601 979 3674.  
E-mail address: [zikri.arslan@jsums.edu](mailto:zikri.arslan@jsums.edu) (Z. Arslan).

Co(II) also enhanced Cd vapor generation modestly (ca. 7-fold) with 8-hydroxyquinoline and 1,10-phenanthroline [22], but as for thiourea, Cu(II), Pb(II) and Bi(III), Ag(I) degraded the performance substantially.

Among the chelating agents utilized, KCN is probably the most effective reagent alleviating the depressive effects of ubiquitous Cu(II), Ni(II), Zn(II) and Pb(II) [11,23,24]. Cyanide ion ( $\text{CN}^-$ ) forms strong complexes with Cu(II), Ni(II) and Zn(II), while cyanides of Pb(II) are very insoluble, that is,  $\text{CN}^-$  acts as releasing agent for Cd(II) in solution. Nevertheless, the improvement with  $\text{CN}^-$  alone was also very modest because of the poor efficiency of Cd vapor generation without a suitable catalyst [23,24]. Co(II) and Ni(II) could not be used with  $\text{CN}^-$  since these elements at higher concentrations form insoluble precipitates (cobalt and nickel borides) upon reaction with  $\text{NaBH}_4$  [15,21]. We also verified this phenomenon in our previous studies (data not published) that the reaction of a mixture of 0.005 M (ca.  $300 \mu\text{g mL}^{-1}$ ) Co(II) or Ni(II) and 0.5% (*m/v*) KCN with  $\text{NaBH}_4$  resulted in dark precipitation along borohydride reaction line rendering the CVG system unusable without vigorous cleaning. On the other hand, cyanide complexes of trivalent transition metal ions, such as Cr(III) and V(III) were found to improve efficiency of Cd vapor generation substantially [25,26]. Moreover, unlike thiourea and L-cysteine systems, the procedures did not experience any deleterious effects from Cu(II), Ni(II), Zn(II), or Pb(II).

In an attempt to further Cd vapor generation, a novel approach is described in this study utilizing titanium (III) and titanium (IV), Ti(III) and Ti(IV), as catalytic additives for efficient generation of volatile Cd species. In a continuous flow system, effects of Ti(III) and Ti(IV) on Cd vapor generation were examined in the presence of thiourea, L-cysteine and KCN for Cd(II) solutions acidified with HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The concentrations of Ti(III), Ti(IV), KCN, and  $\text{NaBH}_4$  solutions, flow rates as well as lengths of mixing tubings were examined in suitable acid medium to determine optimal conditions. The effects of common transition metal ions and hydride forming elements were thoroughly investigated to elucidate the tolerance of the procedures to chemical interferences. The analytical performance of the method was validated by determination of Cd from various certified reference materials by CVG-ICP-MS.

## 2. Experimental

### 2.1. Reagents, standards, and samples

All standard and reagent solutions were prepared with double deionized water with minimum resistivity of  $18.2 \text{ M}\Omega \text{ cm}$  obtained from a Barnstead E-Pure system fed by a reverse-osmosis unit (SpectraPure). Trace-metal grade hydrochloric acid (HCl, BDH Chemicals), nitric acid ( $\text{HNO}_3$ , BDH Chemicals) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , BDH Chemicals) were purchased from VWR International (Suwanee, GA). Titanium (III) sulfate solution ( $\text{Ti}_2(\text{SO}_4)_3$ , 20% (*w/w*) in 2.7%  $\text{H}_2\text{SO}_4$ , Alfa Aesar, Lot No: I20W045), thiourea (98%, Alfa Aesar, Lot No: A12828) and potassium cyanide (KCN, Acros Organics, 97 + % extra pure, Lot No: A0326455) were purchased from Fisher Scientific (Pittsburgh, PA). Titanium (IV) oxysulfate solution ( $\text{TiOSO}_4$ , 99.99%, ~15% (*w/w*) in 5–10%  $\text{H}_2\text{SO}_4$ , Lot No: MKBH3974V), sodium borohydride (98%, Lot No: 05024JH), and L-cysteine (97%, Lot No: 05024JH) were purchased from Sigma Aldrich (St. Louis, MO).

Test solutions of Ti(III) and Ti(IV) were prepared freshly each day by diluting appropriate volume of stock solutions with 0.5% (*v/v*)  $\text{H}_2\text{SO}_4$ . Sodium borohydride ( $\text{NaBH}_4$ ) solution was prepared daily in 0.1% (*m/v*) sodium hydroxide (NaOH) solution (BDH Chemicals). Single element stock standard solutions ( $1000 \mu\text{g mL}^{-1}$ ) were purchased from SPEX Certiprep (Metuchen, NJ). A secondary multielement stock solution consisting of hydride and vapor forming elements,  $10.0 \mu\text{g mL}^{-1}$  of As, Cd, Hg, Pb, Se, and Te, and  $1.0 \mu\text{g mL}^{-1}$  of Ge, Sb, Sn and Bi, was prepared from single element solutions and stored in 2% (*v/v*) HCl + 2% (*v/v*)  $\text{HNO}_3$ . This solution was designated as "CVG stock standard" and used for preparation of all running solutions and calibration standards. Solutions of other trace

elements, including Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, and Zn, were either prepared from high-purity salts or from  $1000 \mu\text{g mL}^{-1}$  stock solutions (Spex Certiprep). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 99.999%, Sigma Aldrich, Lot No: 09327LE) was used with  $\text{HNO}_3$  in digestion of tissue samples.

Five standard certified reference materials (SRM or CRM) were used for method validation. Nearshore seawater (CASS-4), and Dogfish liver (DOLT-4) certified reference materials were purchased from National Research Council Canada (CNRC). Bone ash (SRM 1400), Mussel tissue (SRM 2976) and Domestic sludge (SRM 2781) standard reference materials were obtained from National Institutes of Science and Technology (NIST, Gaithersburg, MD).

### 2.2. Instrumentation and CVG manifold

A Varian 820MS ICP-MS instrument (Varian, Australia) equipped with a peltier-cooled double-pass glass spray chamber, a quartz torch, and standard Ni sampler and skimmer cones was employed in this work. The instrument was optimized in nebulization mode for sensitivity, doubly charged ions (<2%) and oxides (<3%) with  $5 \mu\text{g L}^{-1}$  solution of  $^{138}\text{Ba}$ ,  $^{25}\text{Mg}$ ,  $^{115}\text{In}$ ,  $^{140}\text{Ce}$ , and  $^{208}\text{Pb}$  before vapor generation measurements. Then, CVG manifold was connected to the spray chamber as shown in Fig. 1. The flow rates of argon gas and sampling depth were further examined and optimized for CVG. The operating parameters of the instrument are summarized in Table 1. Data collection was achieved by ICP-MS Expert software package (version 2.2b126). Four isotopes of Cd ( $^{110}\text{Cd}$ ,  $^{111}\text{Cd}$ ,  $^{112}\text{Cd}$  and  $^{114}\text{Cd}$ ) were monitored during the optimization of experimental conditions. Information from major isotopes ( $^{112}\text{Cd}$  and  $^{114}\text{Cd}$ ) were not used due to significant isobaric interferences from  $^{112}\text{Sn}$  and  $^{114}\text{Sn}$  that also form volatile tin hydride ( $\text{SnH}_4$ ). Consequently, all results provided herein are based on  $^{110}\text{Cd}$  and  $^{111}\text{Cd}$  isotopes that are free from isobaric overlaps of Sn isotopes.

The Scott-type double pass glass spray chamber (100 mL inner volume) of the ICP-MS instrument was utilized as gas-liquid separator (GLS). The schematic representation of the CVG manifold and spray chamber is shown in Fig. 1. A polypropylene T-piece (1/8" i.d., 1/4" o.d.) purchased from a local hardware store was modified to fit through the nebulizer housing on the Teflon end-cap of the spray chamber. A 12-cm long PTFE transfer line (1.6 mm i.d. & 1.8 mm o.d.) was inserted through the T-piece extending into the spray chamber. The outer end of the T-piece was sealed tightly to prevent gas leak. Carrier gas was supplied from the nebulizer argon port of the instrument through the lower arm of T-piece (Fig. 1). Three peristaltic pumps were used with the following tygon pump tubings to deliver solutions and remove waste; sample and  $\text{NaBH}_4$ : red-red stop (1.14 mm i.d.); Ti(III) and Ti(IV) and KCN: black-black stop (0.76 mm i.d.); waste: purple-white stop (2.79 mm i.d.). The MC-1 (5 cm, 1.0 mm i.d. PTFE) is designated for mixing of KCN with Ti(III) or Ti(IV). MC-2 (15 cm, 1.0 mm i.d. PTFE) is utilized for mixing the sample solution with premixed Ti(III)–KCN or Ti(IV)–KCN mixture. Until optimization, the lengths of MC-1 and MC-2 were tentatively adjusted to 15 and 20 cm, respectively. While KCN is stable in water, it produces toxic hydrogen cyanide (HCN) upon reaction with mineral acids. Therefore, addition of KCN directly into acidic sample solutions is not recommended due to health hazards from inhalation of HCN vapors. In this CVG manifold setup, KCN solution was prepared in water and reacted with HCl or  $\text{HNO}_3$  in a totally sealed system. The waste containing toxic cyanide species were collected and neutralized in alkaline sodium hydroxide environment in waste container.

### 2.3. Preparation of samples

CASS-4 samples (5 mL) were taken from the bottled stock and acidified to 4% (*v/v*) HCl (0.48 M) with concentrated HCl. Another set of CASS-4 (5 mL) were acidified to 2% (*v/v*)  $\text{HNO}_3$  (0.3 M) with concentrated  $\text{HNO}_3$ . All other powdered SRM samples were digested according to the protocols described previously [25,26]. Approximately 50 mg sub-

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