Published in final edited form as:

Microchem J. 2015 November 1; 123: 170–178. doi:10.1016/j.microc.2015.06.006.

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^{a,*}, Vedat Yilmaz^{a,b}, and LaKeysha Rose^a

^aJackson State University, Department of Chemistry and Biochemistry, Jackson, MS 39217 USA

^bErciyes University, Faculty of Pharmacy, Department of Analytical Chemistry, 38039 Kayseri, Turkey

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 H₂SO₄. Optimum CVG conditions were 4% (v/v) HCl + 0.03 M Ti(III) + 0.16 M KCN and 2% (v/v) HNO₃ + 0.03 M Ti(IV) + 0.16 M KCN with a 3% (m/v) NaBH₄ 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⁻¹ was achieved with Ti(III) by CVG-ICP-MS. The LOD with Ti(IV) was 6.4 ng L⁻¹ 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 NaBH₄ 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⁻¹. Among the hydride forming elements, no interference was observed from As(III) and Se(IV) at 0.5 µg mL⁻¹ level. The depressive effects from Pb(II) and Sb(III) were not significant at 0.1 µg mL⁻¹ 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).

[†]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, zikri.arslan@jsums.edu (Z. Arslan).

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Keywords

Cadmium; Chemical vapor generation; Titanium (III); Titanium (IV); Inductively coupled plasma mass spectrometry

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_4), whereas the latter used aqueous solution with sodium tetraethylborate (NaBEt_4).

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_3 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]. 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 (CN^-) forms strong complexes with Cu(II), Ni(II) and Zn(II), while cyanides of Pb(II) are very insoluble, that is, CN^- acts as releasing agent for Cd(II) in solution. Nevertheless, the improvement with 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 CN^- since these elements at higher concentrations form insoluble precipitates (cobalt and nickel borides) upon reaction with 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 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, HNO_3 and H_2SO_4 . The concentrations of Ti(III), Ti(IV), KCN, and 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 (HNO_3 , BDH Chemicals) and sulfuric acid (H_2SO_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% H_2SO_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 (TiOSO_4 , 99.99%, ~15% (w/w) in 5–10% H_2SO_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) H_2SO_4 . Sodium borohydride (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) 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 (H_2O_2 , 99.999%, Sigma Aldrich, Lot No: 09327LE) was used with 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}Ba , ^{25}Mg , ^{115}In , ^{140}Ce , ^{208}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}Cd , ^{111}Cd , ^{112}Cd and ^{114}Cd) were monitored during the optimization of experimental conditions. Information from major isotopes (^{112}Cd and ^{114}Cd) were not used due to significant isobaric interferences from ^{112}Sn and ^{114}Sn that also form volatile tin hydride (SnH_4). Consequently, all results provided herein are based on ^{110}Cd and ^{111}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 are 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. 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 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 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) HNO₃ (0.3 M) with concentrated HNO₃. All other powdered SRM samples were digested according to the protocols described previously [25,26]. Approximately 50 mg sub-samples (n = 4) of DOLT-4 and SRM 2976 were digested with 3 mL HNO₃ + 1 mL H₂O₂ mixture in 60-mL screw-capped PTFE tubes (Savillex, Eden Prairie, MN) at 140 °C for 2 h on a DigiPrep graphite digestion block (SCP Science, Champlain, NY). At the end of 2-h digestion, the caps were opened and 2 mL of H₂O₂ were added to hot solutions to successfully destroy the organic material. Domestic sludge (SRM 2781) is composed of siliceous matrix and thus was digested using hydrofluoric acid (HF). About 50 mg sub-sample (n=4) was placed in 60-mL PTFE tube and digested in 3 mL HNO₃ + 1 mL HF mixture for 2 h. Bone ash (SRM 1400) is a calcium phosphate matrix. A 100-mg sub-sample (n=4) was readily dissolved with 1 mL HNO₃ in 4-mL PTFE tubes by heating at 110 °C on DigiPrep Cube graphite digestion block (SCP Science, Champlain, NY).

After successful dissolution, solutions of DOLT-4, SRM 2976, SRM 2781 and SRM 1400 were then heated to near dryness; then redissolved with 1 or 2 mL deionized water and heated to near dryness again to get rid of excess HNO₃, H₂O₂ or HF. At the end, the digests were dissolved with small volume of 0.1% (v/v) HNO₃ by heating gently, then diluted to 10 mL with water and stored for analysis. For instrumental analysis, appropriate volumes were pipetted from the stock solutions and further diluted to 10 mL or 50 mL with 4% (v/v) HCl or 2% (v/v) HNO₃.

3. Results and discussion

3.1. Effects of Ti(III) and Ti(IV) on Cd vapor generation

Thiourea, L-cysteine and KCN react with NaBH₄ to form hydroborane and cyanoborane species that are considered to be more effective in hydride transfer to the metal ion than the direct reaction of NaBH₄ with metal ion [16,17,31]. The role of transition metal ions, such as Ni(II) and Co(II), used with thiourea or L-cysteine is also explained with their catalytic activity resulting in more efficient hydrolysis of NaBH₄ for improved hydride transfer to the metal ion [11,14,16,17]. Within this framework, the performances of 0.1 M aqueous solutions of thiourea, L-cysteine and KCN were examined with and without Ti(III) and Ti(IV) on Cd vapor generation using the CVG manifold shown in Fig. 1 for a series of 10 µg L⁻¹ multielement solutions (e.g. As, Cd, Hg, Pb, Se, Te, Ge, Sb, Sn and Bi) within a acidity gradient of 0 to 10% (v/v) HCl (e.g., 0 to 1.2 M HCl) and HNO₃ (0 to 1.5 M HNO₃), and 0 to 5% (v/v) H₂SO₄ (0 to 0.9 M H₂SO₄). The results are provided in Fig. 2. In the absence of Ti(III) or Ti(IV), best signals were observed in HCl medium (Fig. 2A). The results showed that the efficiency of the ligands was in the order of KCN > thiourea > no additive > L-cysteine. Without any ligand, Cd signals were almost equivalent to those with direct nebulization of 10 µg L⁻¹ Cd(II) solution, indicating that direct reaction of NaBH₄ with

Cd(II) was ineffective for generating volatile Cd species. KCN afforded as high as 6-fold (550K to 600K cps) enhancement, whereas that for thiourea was about 2-fold in comparison to that without any ligand. No significant enhancement occurred with L-cysteine regardless of the acidic media.

In the second stage of preliminary studies, 0.04 M Ti(III) or Ti(IV) solution was mixed on-line with thiourea, L-cysteine and KCN along the MC-1 line (Fig. 1) to affect the performances of the ligands on Cd vapor generation. The results are illustrated through Figs. 2B, C and D. The effects of Ti(III) and Ti(IV) varied with the type of acid, but for all three ligands the efficacy of vapor generation was significantly improved. The highest enhancement occurred in the presence of KCN followed by thiourea. Ti(III) + KCN mixture enhanced Cd signals as high as 8-fold and about 45-fold with respect to that with KCN and without any ligand, respectively (see Figs. 2B and A). Optimum working solutions appeared to be either HCl or HNO₃. Signals in H₂SO₄ solutions were comparatively lower. Ti(III) and Ti(IV) also boosted the Cd signals when mixed with thiourea, but not as efficiently as for KCN. Ti (III) + thiourea (TU) was most influential in HCl and H₂SO₄ medium (Figs. 2B and D), whereas Ti(IV) + thiourea affected the vapor generation in HNO₃ solution (Fig. 2C). Cd signals increased about 4-fold in comparison to those with 0.1 M thiourea solution. These results were similar to those observed for thiourea + Co(II) system [11,14,15,21], and were indicative of catalytic effect of Ti(III) and Ti(IV) on the generation of volatile Cd species. For L-cysteine, Ti(III) provided marginal increase in Cd signals in H₂SO₄ medium (Fig. 2D), while Ti(IV) had no significant effect; nor was any improvement observed from Ti(III) or Ti(IV) in HCl or HNO₃.

3.2. Verification and optimization of CVG conditions with KCN

It was also evident from the preliminary studies that Ti(III) and Ti(IV) affected the vapor generation differentially with KCN. Specifically, Ti(III) enhanced signals in HCl, while Ti(IV) was more effective in HNO₃. To verify this phenomenon, additional experiments were carried out independently for Cd solutions (10 µg L⁻¹) prepared in HCl and HNO₃. The results were consistent as shown in Fig. 3. Ti(III) contributed most to the enhancement of Cd vapor generation in HCl medium. CVG performance decreased by two-fold in HNO₃ even though Cd signals increased significantly. In contrast, Ti(IV) was most effective in HNO₃ medium, and its performance declined in HCl medium. Visual observations suggested that this discrepancy was associated with the stability of Ti(III) and Ti(IV) in the particular acid medium. Ti(III) solution prepared in dilute HNO₃ was the least stable developing colloidal solution rapidly. Running solutions prepared in water without additional H₂SO₄ were also unstable developing white colloids (i.e., TiO₂ colloids) within a few hours. On the other hand, experimental solutions acidified with dilute H₂SO₄ (0.5 or 1% (v/v) H₂SO₄) were stable overnight. Ti(IV), TiOSO₄, solutions were relatively more stable, but formation of TiO₂ colloids were noted overnight. Therefore, both Ti(III) and Ti(IV) were prepared freshly from stocks daily in 0.5% or 1% (v/v) H₂SO₄.

The optimum acid concentration ranged from 3 to 5% (v/v) HCl (e.g., 0.36 to 0.6 M) for Ti(III) + KCN system with an optimum at around 4% (v/v) HCl (0.48 M). For Ti(IV) + KCN system, the range was narrower between 2 and 3% (v/v) HNO₃ (e.g., 0.3 to 0.45 M

HNO₃) for which optimum working concentration appeared to be around 2% (v/v) HNO₃ (0.3 M). The working range in previous studies also varied with the acid of choice, but was narrower. For instance, Guo and Guo [11] reported an optimum range between 0.22 to 0.28 M HCl (ca. 1.8–2.3% HCl) and Chuachud and Tyson [15,21] utilized a range between 0.25 – 0.30 M HNO₃ (ca. 1.7 – 2% HNO₃). Apparently, the range was relatively broad for both HCl and HNO₃ in this study, which was mainly due to the buffer effect by KCN (0.1 M). Consequently, the signal stability was readily maintained under same flow rates for accurate determinations in real samples.

3.3. Optimization of KCN, Ti(III) and Ti(IV) concentrations

The concentration of KCN was examined between 0 and 0.3 M (e.g., 0 to 2% m/v) using the optimum acid medium for 0.04 M Ti(III) and Ti(IV) and the results are shown in Fig 4A. Cd signals increased rapidly with 0.05 M KCN and reached a maximum at 0.1 M. The optimum range was between 0.1 and 0.2 M KCN. Signals declined when KCN levels increased above 0.2 M. No significant depressive effects were observed from KCN in previous studies [25,26]; on the contrary, stability was better with higher KCN levels as it afforded effective masking of the interferences from other ionic species. Yet, with Ti(III) and Ti(IV), increasing KCN levels led to precipitation of colloidal TiO₂ along the reaction lines, which was virtually insoluble when mixed with acidic sample solution. The deposition was even more evident along the MC-1 tubing where KCN interacted with Ti(III) or Ti(IV) solution first. It was assumed that colloidal TiO₂ formed along the MC-2 line when KCN levels were raised above 0.2 M resulting in loss of Ti(III) or Ti(IV) from the reaction medium. This hurdle was avoided by minimizing the length of the MC-1 tubing, which is discussed below.

To optimize Ti(III) and Ti(IV) concentration, KCN concentration was adjusted to 0.16 M. As shown in Fig. 4B, Cd signals increased sharply with increasing Ti(III) and Ti(IV) concentration up to 0.03 M and then exhibited a plateau up to 0.08 M, above which signals declined as occurred for KCN. Optimum range was between 0.03 to 0.06 M for both Ti(III) and Ti(IV). A second deposition was observed at the connection of the transfer line when sample solution containing Ti(III) or Ti(IV) interacted with NaBH₄. Unlike white deposition on MC-1 tubing, this deposition was dark violet for Ti(III) and white for Ti(IV); indicative of formation of oxides (Ti₂O₃ and TiO₂), respectively. Dark-violet deposits were readily removed during the fast runs between replicate measurements, but TiO₂ colloids were stickier on the PTFE transfer line. Nevertheless, this deposition did not impact the vapor generation under the operating conditions, and Cd signals steadily increased up to 0.08 M Ti(III) or Ti(IV). The reduction in signals was thought to associate with inhibition of hydrolysis of NaBH₄ by excessive precipitation rather than chemical suppression of Ti(III) or Ti(IV). It should also be noted that both Ti(III) and Ti(IV) were found to substantially depress the generation of hydrides of interfering elements, such as Pb(II), Bi(III), As(III), Sb(III), and Sn(IV), therefore, the concentrations were raised to 0.05 M for Ti(III) and Ti(IV) and maintained until the examination of the analytical performance figures that is discussed later.

3.4. Mechanism of action

The mixing sequences of the solutions were altered to elucidate the role of Ti(III) and Ti(IV) on Cd vapor generation; whether the reaction is driven by formation of cyanide complexes or purely catalytic. The schemes are shown in Fig. 5. Scheme 1 is the identical with that in Fig. 1 where formation of cyanide complex of Ti(III) or Ti(IV) was aimed prior to interaction with acidic sample solution, whereas in Scheme 2, Cd(II) was complexed with CN^- first, then mixed with Ti(III) or Ti(IV), and finally reacted with NaBH_4 . Despite these differences, Scheme 1 and Scheme 2 showed similar signal profiles for Cd (see Fig. 6), indicating that mixing sequence of KCN did not affect the efficacy of the vapor generation. In other words, the generation of volatile Cd species was virtually independent of the complexation (*viz.* interaction time) of KCN with Ti(III) or Ti(IV), or Cd(II) provided that they were all mixed completely prior to reaction with NaBH_4 . This result was also verified later that similar performances could be achieved by using even shorter MC-1 and MC-2 tubings.

In Scheme 3, Ti(III) or Ti(IV) solution was introduced after the acidic sample solution (e.g., Cd(II)-cyanide complex) was reacted with NaBH_4 , where the processes responsible for Cd vapor generation were initiated prior to addition of Ti(III) or Ti(IV). Signals were still improved, but vapor generation efficacy was significantly lower (Fig. 6); about 4-fold with respect to that with KCN (Fig. 2A). This result confirmed that Ti(III) and Ti(IV) acted as catalyst influencing the hydrolysis of NaBH_4 and consequently the yield of reactive cyanoborane intermediates. The marginal enhancement observed with KCN also supports this explanation that NaBH_4 was hydrolyzed inefficiently in the absence of Ti(III) or Ti(IV). The reduction in vapor generation efficacy in Scheme 3 is likely due to the loss of reactive intermediates along the MC-2 line before interaction with the catalyst, which in due course suggests that Ti(III) or Ti(IV) must be introduced to the sample solution prior to reaction with NaBH_4 to achieve the optimum enhancement.

3.5. Effects of lengths of mixing tubings

The lengths of the MC-1 and MC-2 tubings were studied from 5 to 40 cm (1.0 mm i.d. PTFE) at the optimum conditions. The MC-2 tubing was kept at 20 cm to optimize that of MC-1. Variation in signals was not significant up to 20-cm long MC-1 tubing. Both Ti(III) and Ti(IV) yielded white deposition on the walls of MC-1 tubing upon mixing with KCN. The deposition was more intense for longer tubings due to prolonged interaction of Ti(III) or Ti(IV) solution with KCN. In addition, signals tended to decline above 25 cm; for 40-cm tubing Cd signal dropped as much as 20%. To minimize this deposition, the length of MC-1 tubing was reduced to 5 cm and the effect of the length of MC-2 tubing was examined. The length of the MC-2 tubing had no effect on Cd signals when varied from 5 to 40 cm, nor was any precipitation observed with up to 40 cm. In practical analysis, sample solutions possess complex matrices of transition metals that should be masked fully to eliminate possible chemical interferences on vapor generation. Thus, a 15-cm long line was considered to be optimum to ensure sufficient interaction time for the formation of cyanide complexes of transition metals.

3.6. Optimization of flow rates and NaBH₄ concentration

The flow rates of the reagents were not modified throughout the study; only that of sample solution was varied from 0.5 to 2.5 mL min⁻¹. Cd signals increased almost linearly with increasing flow rate up to 2.0 mL min⁻¹, and then leveled off slightly at 2.5 mL min⁻¹. The sample consumption was substantial and was not practical for ICP-MS analysis at 2.0 mL min⁻¹; therefore, the flow rate of the sample solution was kept the same at 1.0 mL min⁻¹. The effect of NaBH₄ was examined between 0.5 and 4% (m/v) NaBH₄ solutions prepared in 0.1% (m/v) NaOH. Highest signals were achieved with 2 to 3% (m/v) NaBH₄. Signals declined between 3.5 and 4.0% (m/v) NaBH₄, which was due to the change in the sampling zone in the plasma since gaseous by-products (e.g., H₂) from decomposition of NaBH₄ increased the carrier argon flow rate. The length of the NaBH₄ line (1.6 mm i.d. PTFE tubing) was varied from 12 to 20 cm to affect the vapor generation efficiency. Surprisingly, the best performance was observed with 12 cm tubing which was also the shortest transfer line allowing transfer of gaseous products into the spray chamber. Signals were lower, especially with 20 cm transfer line. This result indicated that volatile Cd species were relatively unstable and thus had to be separated from the reaction environment as quickly as possible. The carrier argon flow rate was also critical to control the sampling zone precisely. Suitable range was often between 1.1 and 1.2 L min⁻¹ with an optimum at 1.15 L min⁻¹.

3.7. Effects of chemical interferences

The interferences from transition metals and hydride forming elements were examined under the optimized conditions and the results are summarized in Table 2. No significant suppression was observed from common transition metals ions, including Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), and Zn(II) up to 1.0 µg mL⁻¹ test concentrations that were 100-fold above that of Cd(II). Relative responses varied between 96% (Cr) and 101% in HCl-Ti(III)-KCN medium, and between 92% (Ni) and 103% (Zn) for HNO₃-Ti(IV)-KCN. Co(II) is usually known to enhance Cd signals in CVG procedures at around 1 to 10 µg mL⁻¹ levels, but no significant enhancement occurred with Ti(III) nor with Ti(IV). The effects of most severely interfering Cu(II) and Ni(II) were also insignificant in Ti(III)-KCN environment. The responses in Ti(IV)-KCN were slightly lower; 93% for Cu(II) and 92% for Ni(II), which could point to reduced masking ability of KCN or vapor phase interferences from these elements in HNO₃ medium.

Signals profiles of hydride forming elements (As, Bi, Pb, Sb, Se, Sn) were also monitored in the working solutions during the course of the preliminary studies. While enhancing Cd vapor generation, both Ti(III) and Ti(IV) substantially suppressed the signals of these elements as much as 50–60%. Accordingly, the hydride forming elements showed depressive effects on Cd vapor generation unlike the transition metal ions. As(III) and Se(IV) were the most benign when their concentrations were raised up to 0.5 µg mL⁻¹. Bi(III), Pb(II) Sb(III) and Sn(II) suppressed signals at the same concentrations significantly. The effects from Pb(II) and Sb(III) were not significant at 0.1 µg mL⁻¹ levels; the responses were between 96% and 103% for Ti(III) and Ti(IV). Bi(III) and Sn(II) were the most strongly interfering elements; in the presence of 0.1 µg mL⁻¹ Bi(III) or Sn(II), Cd signals were around 80 and 86% in HCl-Ti(III)-KCN and were 98% in HNO₃-Ti(IV)-KCN. It was evident that HNO₃-Ti(IV)-KCN was more tolerant to Bi(III) and Sn(II) than HCl-Ti(III)-

KCN, which was attributed to better stabilization of Ti(IV) in HNO₃ medium. Despite these interferences, the methods appear to be highly robust in practical analysis because of the fact that the interfering elements are found in most samples at low parts per billion levels; and therefore, are not expected to pose any risks in Cd determinations by CVG-ICP-MS.

3.8. Analytical figures of merit

Solutions of Ti(III), Ti(IV) and KCN (0.1 M each) were tested for Cd blanks by ICP-OES. No significant Cd impurities were detected. KCN was found to be ultrapure. Despite this, the blank signals in CVG-ICP-MS ranged between 20K and 28K cps in the presence of 0.05 M Ti(III) and Ti(IV) solutions. Additional trials verified that blank signals were mainly from Cd impurities present at low parts per trillion (ppt) levels in Ti(III) and Ti(IV) solutions, especially in Ti(IV) solution. Consequently, the concentrations of Ti(III) and Ti(IV) were reduced to 0.03 M which appeared to be the lowest optimum level (see Fig 4B). Under these conditions, the limit of detection (LOD, 3s, n = 14) was 3.4 and 3.2 ng L⁻¹ for ¹¹⁰Cd and ¹¹¹Cd isotopes, respectively, in HCl-Ti(III)-KCN medium while those in HNO₃-Ti(IV)-KCN medium were relatively higher; 6.3 and 6.4 ng L⁻¹ for ¹¹⁰Cd and ¹¹¹Cd, respectively (n = 14). Precision for 6 replicate measurements (%RSD) varied between 0.4% and 7% within a range of 0.02 to 10 µg L⁻¹ Cd(II). The natural abundances of ¹¹⁰Cd (12.49%) and ¹¹¹Cd (12.80%) are relatively similar. As a result, the LODs obtained with ¹¹⁰Cd and ¹¹¹Cd isotopes did not differ significantly from each other. Nevertheless, there is an isobaric overlap on ¹¹⁰Cd from ¹¹⁰Pd (11.72%), which could lead to inaccuracy in Cd determinations from samples containing significant levels of (palladium (Pd)). Therefore, ¹¹¹Cd appears to be the preferred isotope.

Typical calibration curves constructed using 4% (v/v) HCl + 0.03 M Ti(III) + 0.16 M KCN and 2% (v/v) HNO₃ + 0.03 M Ti(III) + 0.16 M KCN are shown in Fig. 7 along with that obtained with direct nebulization of the same standard solutions within 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10 µg L⁻¹ Cd(II). The calibration sensitivity (e.g., slope of the calibration) was 5.871×10^5 cps ppb⁻¹ for Ti(III) and 5.189×10^5 cps ppb⁻¹ for Ti(IV). The approach afforded an improvement of 40-fold with Ti(III) and 35-fold with Ti(IV) based on the ratios of the calibration sensitivity with CVG to that of nebulization ICP-MS. These values are by far the highest enhancement factors achieved to date for chemical vapor generation of Cd. The enhancement factors could be increased further by using higher flow rates up to 2 mL min⁻¹ but at the cost of increased sample consumption. For cleaning, a fast wash at 5 mL min⁻¹ was performed between samples for 20 s with 4% (v/v) HCl or 2% (v/v) HNO₃ depending the medium of analysis, which was sufficient to remove the residual sample and vapor within the sample line and spray chamber. Under the optimized operating conditions, the methods afforded a sampling frequency of 35 samples h⁻¹.

3.9. Validation of the methods

The procedures were validated by analysis of five different certified reference materials. Application to brines was performed with seawater (CASS-4) which was directly analyzed by adjusting the acidity of 5-mL sub-samples (n=4) to 4% (v/v) HCl (e.g., 0.48 M HCl) and 2% (v/v) HNO₃ (e.g., 0.3 M HNO₃). Previously prepared 10-mL stock solutions of other SRMs were further diluted to adjust Cd concentration in solution within the calibration

range (e.g., 0.02 to 5 $\mu\text{g L}^{-1}$). To do this, 1.0 mL from DOLT-4 and SRM 2781 stocks were taken and diluted to 25 mL with 4% (v/v) HCl or 2% (v/v) HNO_3 . For SRM 2976, 1.0 mL from its stock was diluted to 10 mL with 4% (v/v) HCl or 2% (v/v) HNO_3 . For SRM 1400, 10-mL stock solutions were split into two 5 mL, and each was completed to 10 mL with either 4% (v/v) HCl or 2% (v/v) HNO_3 . The results obtained from the analysis of certified reference materials (CRMs) are summarized in Table 3. The concentrations determined in CASS-4 agreed with the certified values. No interferences were observed from alkali (Na and K) and alkaline earth elements (Ca and Mg) in seawater matrix. Residual H_2O_2 in some DOLT-4 and SRM 2976 samples hampered vapor generation efficiency. Similar effects were also observed in previous studies [25,26] that even trace amounts of H_2O_2 interferes substantially with Cd vapor generation; and therefore, must be removed from samples completely. Additional samples from the stocks were taken and re-heated to dryness to remove residual H_2O_2 , and prepared as described above. Under these conditions, accurate results were obtained for DOLT-4 and SRM 2976. Recoveries ranged between 95 and 105% for DOLT-4, and 91 and 98% for SRM 2976.

The Bone ash (SRM 1400) was composed of calcium phosphate matrix yielding high levels of Ca(II) and phosphate, about 2000 and 2700 $\mu\text{g mL}^{-1}$, respectively, along with 3.3 $\mu\text{g mL}^{-1}$ Fe and 2.6 $\mu\text{g mL}^{-1}$ Al. No significant suppression or enhancement was observed, and low levels of Cd were accurately measured by CVG-ICP-MS. SRM 2781 had the most complex matrix among the samples analyzed, which contained 2.8% Fe, 1.6% Al, 0.6% Mg, 1273 $\mu\text{g g}^{-1}$ Zn, 627 $\mu\text{g g}^{-1}$ Cu, 202 $\mu\text{g g}^{-1}$ Cr and Pb, and 98 $\mu\text{g g}^{-1}$ Ag. These concentrations yielded 5.6 $\mu\text{g mL}^{-1}$ Fe and 3.2 $\mu\text{g mL}^{-1}$ Al in addition to sub-ppm levels of other elements in diluted solutions. The results for Cd were in agreement with certified value within 95% confidence level. Recoveries ranged between 93 to 104% for Ti(III)-KCN and Ti(IV)-KCN combinations.

4. Conclusions

In this study, we have developed a highly sensitive chemical vapor generation method for determination of Cd by utilizing Ti(III) and Ti(IV) as catalytic reagents for the first time. In the presence of KCN, the results proved that they are by far the most effective catalytic additives affording substantial enhancement in Cd vapor generation for accurate determinations at ultratrace levels from saline and complex samples. The methods are in principle suitable for analysis of many complex environmental, biological and pharmacological samples without any need for additional separation approaches, such as ion extraction and coprecipitation etc. The simplicity and robustness of the operational conditions add to the attractiveness of the method besides its remarkable sensitivity. A relatively large working acid range along with high tolerance to chemical interferences ensure flexibility for adapting the method to flame atomic absorption (FAAS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) to carry out sub-ppb determinations with these commonly employed spectroscopy techniques that lack the desired detection power for determination of Cd.

Acknowledgments

This project was supported by grants from the National Institute of Health (NIH), Research Centers in Minority Institutions (RCMI), Center for Environmental Health (CEH) Program (G12 MD007581) and Research Initiative for Scientific Enhancement (RISE) Program (2 R25 GM067122) at Jackson State University. The views expressed herein are those of the authors and do not necessarily represent the official views of the NIH and any of its sub-agencies. The authors also acknowledge financial support from the Scientific and Technological Council of Turkey (TUBITAK) to Dr. Vedat Yilmaz during the course of this project.

References

1. Howard AG. (Boro)Hydride Techniques in Trace Element Speciation. *Journal of Analytical Atomic Spectrometry*. 1997; 12:267–272.
2. Evans EH, Day JA, Palmer C, Price WJ, Smith CMM, Tyson JF. Atomic spectrometry update. Advances in atomic emission, absorption and fluorescence spectrometry, and related techniques. *J Anal At Spectrom*. 2006; 21:592–625.
3. Wu P, He L, Zheng C, Hou X, Sturgeon RE. Applications of chemical vapor generation in non-tetrahydroborate media to analytical atomic spectrometry. *J Anal At Spectrom*. 2010; 25:1217–1246.
4. Evans EH, Pisonero J, Smith CMM, Taylor RN. Atomic spectrometry updates: Review of advances in atomic spectrometry and related techniques. *J Anal At Spectrom*. 2014; 29:773–794.
5. Cacho J, Beltran I, Nerin C. Generation of a volatile cadmium species in an organic medium. *J Anal At Spectrom*. 1989; 4:661–663.
6. D'Ulivo A, Chen YJ. Determination of cadmium in aqueous samples by vapour generation with sodium tetraethylborate(III) reagent. *J Anal At Spectrom*. 1989; 4:319–322.
7. Valdés-Hevia y Temprano MC, Fernández de la Campa MR, Sanz-Medel A. Generation of volatile cadmium species with sodium tetrahydroborate from organized media: application to cadmium determination by inductively coupled plasma atomic emission spectrometry. *J Anal At Spectrom*. 1993; 8:847–852.
8. Valdés-Hevia y Temprano MC, Fernández de la Campa MR, Sanz-Medel A. Sensitive inductively coupled plasma atomic emission spectrometric determination of cadmium by continuous alkylation with sodium tetraethylborate. *J Anal At Spectrom*. 1994; 9:231–236.
9. Sanz-Medel A, Valdés-Hevia y Temprano MC, Bordel García N, Fernández de la Campa MR. The use of surfactants to obtain cadmium atoms at room temperature and its application for the cold vapour AAS determination of the metal. *Anal Proc*. 1995; 32:49–52.
10. Sanz-Medel A, Valdés-Hevia y Temprano MC, Bordel García N, Fernández de la Campa MR. Generation of cadmium atoms at room temperature using vesicles and its application to cadmium determination by cold vapor atomic spectrometry. *Anal Chem*. 1995; 67:2216–2223.
11. Guo X, Guo X. Studies on the reaction between cadmium and potassium tetrahydroborate in aqueous solution and its application in atomic fluorescence spectrometry. *Anal Chim Acta*. 1995; 310:377–385.
12. Matusiewicz H, Kopras M, Sturgeon RE. Determination of cadmium in environmental samples by hydride generation with in situ concentration and atomic absorption detection. *Analyst*. 1997; 122:331–336. [PubMed: 9177076]
13. Feng YL, Sturgeon RE, Lam JW. Generation of atomic and molecular cadmium species from aqueous media. *Anal Chem*. 2003; 75:635–640. [PubMed: 12585495]
14. Lampugnani L, Salvetti C, Tsalev DL. Hydride generation atomic absorption spectrometry with different flow systems and in-atomizer trapping for determination of cadmium in water and urine: overview of existing data on cadmium vapour generation and evaluation of critical parameters. *Talanta*. 2003; 61:683–698. [PubMed: 18969233]
15. Chuachud W, Tyson JF. Determination of cadmium by flow injection atomic absorption spectrometry with cold vapor generation by a tetrahydroborate-form anion-exchanger. *J Anal At Spectrom*. 2005; 20:273–281.

16. D'Ulivo A, Baiocchi C, Pitzalis E, Onor M, Zamboni R. Chemical vapor generation for atomic spectrometry. A contribution to the comprehension of reaction mechanisms in the generation of volatile hydrides using borane complexes. *Spectrochim Acta Part B*. 2004; 59:471–486.
17. D'Ulivo A. Chemical vapor generation by tetrahydroborate(III) and other borane complexes in aqueous media: A critical discussion of fundamental processes and mechanisms involved in reagent decomposition and hydride formation. *Spectrochim Acta Part B*. 2004; 59:793–825.
18. Vargas-Razo C, Tyson JF. Determination of cadmium by flow injection-chemical vapor generation-atomic absorption spectrometry. *Fresenius' J Anal Chem*. 2000; 366:182–190. [PubMed: 11225925]
19. Hwang TJ, Jiang SJ. Determination of cadmium by flow injection isotope dilution inductively coupled plasma mass spectrometry with vapour generation sample introduction. *J Anal At Spectrom*. 1997; 12:579–584.
20. Chang YT, Jiang SJ. Determination of As, Cd and Hg in emulsified vegetable oil by flow injection chemical vapour generation inductively coupled plasma mass spectrometry. *J Anal At Spectrom*. 2008; 23:140–144.
21. Chuachud W, Tyson JF. Determination of cadmium by electrothermal atomic absorption spectrometry with flow injection chemical vapor generation from a tetrahydroborate-form anion-exchanger and in-atomizer trapping. *Can J Anal Sci Spectrosc*. 2004; 49:362–373.
22. Sun H, Suo R. Enhancement reagents for simultaneous vapor generation of zinc and cadmium with intermittent flow system coupled to atomic fluorescence spectrometry. *Anal Chim Acta*. 2004; 509:71–76.
23. Garrido ML, Munoz-Olivas R, Camara C. Interference removal for cadmium determination in waste water and sewage sludge by flow injection cold vapour generation atomic absorption spectrometry. *J Anal At Spectrom*. 1998; 13:1145–1149.
24. Liva M, Munoz-Olivas R, Camara C. Determination of Cd in sonicate slurries and leachates of biological and environmental materials by FI-CV-AAS. *Talanta*. 2000; 51:381–387. [PubMed: 18967870]
25. Yilmaz V, Rose L, Arslan Z, Little MD. On-line chemical vapour generation of cadmium in the presence of hexacyanochromate III for determination by inductively coupled plasma mass spectrometry (ICP-MS). *J Anal At Spectrom*. 2012; 27:1895–1902. [PubMed: 23997384]
26. Yilmaz V, Arslan Z, Rose L, Little MD. Cyanovanadate(III) complexes as novel additives for efficient generation of volatile cadmium species in complex samples prior to determinations by inductively coupled plasma mass spectrometry (ICP-MS). *Talanta*. 2013; 115:681–687. [PubMed: 24014893]
27. Adeloju SB, Zhang Y. Vapor generation atomic absorption spectrometric determination of cadmium in environmental samples with in-line anion exchange separation. *Anal Chem*. 2009; 81:4249–4255. [PubMed: 19402645]
28. Pourreza N, Ghanemi KJ. Solid phase extraction of cadmium on 2-mercaptobenzothiazole loaded on sulfur powder in the medium of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate and cold vapor generation–atomic absorption spectrometric determination. *J Hazard Mater*. 2010; 178:566–571. [PubMed: 20176439]
29. ahan S, ahin U. An automated on-line minicolumn preconcentration cold vapour atomic absorption spectrometer: Application to determination of cadmium in water samples. *Talanta*. 2012; 88:701–706. [PubMed: 22265561]
30. Manzoori JL, Abdolmohammad-Zadeh H, Amjadi M. Ultratrace determination of cadmium by cold vapor atomic absorption spectrometry after preconcentration with a simplified cloud point extraction methodology. *Talanta*. 2007; 71:582–587. [PubMed: 19071344]
31. Pitzalis E, Ajala D, Onor M, Zamboni R, D'Ulivo A. Chemical vapor generation of arsane in the presence of L-cysteine. Mechanistic studies and their analytical feedback. *Anal Chem*. 2007; 79:6324–6333. [PubMed: 17636881]
32. Guo X, Guo X. Determination of cadmium at ultratrace levels by cold vapour atomic absorption spectrometry. *J Anal At Spectrom*. 1995; 10:987–990.

Highlights

- Titanium ions were utilized for the first time as catalytic additives for cadmium vapor generation.
- Ti(III) and Ti(IV) enhanced generation of Cd vapor significantly with KCN.
- Sensitivity was improved by 40-fold with Ti(III) and 35-fold with Ti(IV).
- Method detection limits were as low as 3.2 ng L^{-1} for ^{111}Cd by ICP-MS.

Fig. 1.
Schematic representation of the chemical vapor generation (CVG) manifold. MC-1 and MC-2 are 5- and 15-cm long PTFE tubings (1.0 mm i.d.), respectively.

Fig. 2.

Effects of Ti(III) and Ti(IV) on Cd vapor generation in the presence of thiourea (TU), L-cysteine (L-cys) and KCN in HCl, HNO₃ and H₂SO₄. A: without Ti(III) or Ti(IV); water was run through Ti(III) and Ti(IV) channel. B, C and D: with Ti(III) and Ti(IV). Ti(III) = 0.04 M, Ti(IV) = 0.04 M, Thiourea = 0.1 M, L-cysteine = 0.1 M, KCN = 0.1 M. NaBH₄ = 2% (m/v), MC-1 = 15 cm; MC-2 = 20 cm.

Fig. 3.

Effects of HCl and HNO₃ on the vapor generation profiles of Cd with Ti(III)-KCN and Ti(IV)-KCN mixtures. Cd(II) = 10 µg L⁻¹, Ti(III) = 0.04 M, Ti(IV) = 0.04 M, KCN = 0.1 M, NaBH₄ = 2% (m/v), MC-1 = 15 cm; MC-2 = 20 cm.

Fig. 4. Effects of KCN, Ti(III) and Ti(IV) concentration on the vapor generation of $10\text{ }\mu\text{g L}^{-1}$ Cd. MC-1 = 15 cm, MC-2 = 20 cm, NaBH_4 = 2% (m/v).

Fig. 5. Manifold setups utilized for examining the role of Ti(III) and Ti(IV) on Cd vapor generation. 4% (v/v) HCl + 0.05 M Ti(III) + 0.16 M KCN and 2% (v/v) HNO₃ + 0.05 M Ti(IV) + 0.16 M KCN. MC-1 = 15 cm, MC-2 = 20 cm, NaBH₄ = 2% (m/v).

Fig. 6. Signals profiles from vapor generation of Cd(II) ($10 \mu\text{g L}^{-1}$) using the manifold setups shown in Fig. 5.

Fig. 7.

Typical calibration curves for Cd obtained by CVG-ICP-MS and nebulization ICP-MS.

CVG (HCl): 4% (v/v) HCl + 0.03 M Ti(III) + 0.16 M KCN. CVG (HNO₃): 2% (v/v) HNO₃ + 0.03 M Ti(IV) + 0.16 M KCN. MC-1 = 5 cm, MC-2 = 15 cm, NaBH₄ = 3% (m/v).

Table 1

Operating conditions for ICP-MS and vapor generation system

ICP-MS		Varian 820MS	
RF Power (kW)		1.4	
		Plasma gas	18
		Auxiliary gas	1.8
Argon flow rates (L min ⁻¹)		Nebulizer gas	1.15
		Sheath gas	0.16
Sampling depth (mm)		6	
Spray chamber temperature (°C)		4	
Scan mode		Peak hopping	
Read delay time (s)		45	
Dwell time (ms)		50	
Points/peak		1	
Scans/peak		6	
Scans/replicate		10	
Isotopes		¹¹⁰ Cd, ¹¹¹ Cd	

Vapor generation			
Reagent	Ti(III) setup	Ti(IV) setup	Flow rate (mL min ⁻¹)
Ti ₂ (SO ₄) ₃	0.015 M	-	0.5
TiOSO ₄	-	0.03 M	0.5
Acid	4% (v/v) HCl (0.48 M)	2% (v/v) HNO ₃ (0.3 M)	1.0
KCN	0.16 M	0.16 M	0.5
NaBH ₄	3% (m/v)	3% (m/v)	1.0

Table 2

Effects of transition metals and hydride forming elements on Cd vapor generation in Ti(III) - KCN and Ti(IV) - KCN media

Transition metals	Concentration ($\mu\text{g mL}^{-1}$)	Relative response (%) ^a	
		HCl Ti(III) - KCN	HNO ₃ Ti(IV) - KCN
Co(II)	1.0	99 ± 4	99 ± 4
Cr(III)	1.0	96 ± 4	99 ± 3
Cu(II)	1.0	99 ± 3	93 ± 5
Fe(III)	1.0	101 ± 3	99 ± 2
Mn(II)	1.0	101 ± 5	98 ± 3
Ni(II)	1.0	102 ± 2	92 ± 4
Zn(II)	1.0	101 ± 3	103 ± 5
Hydride forming elements			
As(III)	0.5	104 ± 6	102 ± 7
Bi(III)	0.1	80 ± 3	98 ± 3
	0.2	62 ± 5	84 ± 4
	0.5	46 ± 5	61 ± 5
Pb(II)	0.1	102 ± 4	96 ± 2
	0.2	82 ± 4	88 ± 4
	0.5	50 ± 3	75 ± 3
Sb(III)	0.1	103 ± 3	102 ± 4
	0.2	77 ± 5	72 ± 3
	0.5	64 ± 4	60 ± 5
Se(IV)	0.5	96 ± 2	92 ± 4
Sn(II)	0.1	86 ± 2	98 ± 5
	0.2	67 ± 4	78 ± 2
	0.5	32 ± 3	46 ± 4

^a Values are ratio of average ± standard deviation of three replicate measurements in the presence of matrix element to that of 10 $\mu\text{g L}^{-1}$ Cd(II) solution only.

Table 3

The results from determination of Cd in standard reference materials by CVG-ICP-MS. Concentrations are $\mu\text{g g}^{-1}$ for all, except CASS-4 for which values are $\mu\text{g L}^{-1}$.

Sample	Isotope	Found ^a		Certified value
		HCl - Ti(III) - KCN	HNO ₃ - Ti(IV) - KCN	
Nearshore seawater (CASS-4)	¹¹⁰ Cd	0.024 ± 0.004	0.027 ± 0.003	0.026 ± 0.003
	¹¹¹ Cd	0.024 ± 0.004	0.026 ± 0.006	
Bone ash (SRM 1400)	¹¹⁰ Cd	0.026 ± 0.002	0.023 ± 0.005	(0.03)
	¹¹¹ Cd	0.024 ± 0.002	0.026 ± 0.007	
Dogfish liver (DOLT-4)	¹¹⁰ Cd	23.1 ± 1.1	25.0 ± 0.8	24.3 ± 0.8
	¹¹¹ Cd	23.2 ± 0.9	25.6 ± 1.2	
Mussel tissue (SRM 2976)	¹¹⁰ Cd	0.78 ± 0.04	0.80 ± 0.14	
	¹¹¹ Cd	0.75 ± 0.06	0.81 ± 0.09	0.82 ± 0.16
Domestic sludge (SRM 2781)	¹¹⁰ Cd	12.0 ± 1.2	13.1 ± 0.8	12.78 ± 0.72
	¹¹¹ Cd	11.9 ± 1.2	13.3 ± 0.7	

^a Values are given as mean ± standard deviation of four replicate analyses. Values in parenthesis are “information only.”