Talanta 115 (2013) 681–687

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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)

Vedat Yilmaz [a,b], Zikri Arslan [a,*], LaKeysha Rose [a], Maria D. Little [a]

[a] Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS, USA
[b] Department of Analytical Chemistry, Faculty of Pharmacy, Erciyes University, Kayseri, Turkey

ARTICLE INFO

Article history:
Received 2 April 2013
Received in revised form
23 June 2013
Accepted 24 June 2013
Available online 28 June 2013

Keywords:
Cadmium
Vapor generation
Hexacyanovanadate(III) complex
On-line generation
ICP-MS

ABSTRACT

A new method has been described for generation of volatile species of Cd using vanadium(III) cyanide complex. Aqueous solutions of 0.04 mol L^{-1} vanadium chloride (VCl_3) and 0.12 mol L^{-1} potassium cyanide (KCN) were reacted on-line yielding a suspension of vanadium hydroxide, $V(OH)_3$. This suspension was dissolved along the stream of sample solution in dilute HCl to form heptacyanovanadate(III) complex, $[V(CN)_7]^{4-}$. Volatile Cd species were generated by reacting the stream of sample solution and cyanovanadate(III) complex with sodium borohydride ($NaBH_4$). Feasibility of off-line and on-online approaches was investigated for quantitative determinations. Better precision and daily stability were achieved with on-line settings. Optimum signals were obtained from sample solutions within a range of 3 to 5% v/v HCl. A concentration of 2% m/v $NaBH_4$ was adequate to achieve an enhancement of 20-fold in the presence of cyanovanadate(III) complex. The limits of detection were 5.0 and 4.5 ng L^{-1} for ^{110}Cd and ^{111}Cd isotopes, respectively. Precision (%RSD) was better than 4.7% for six replicate measurements. The interferences of Cu(II) and Ni(II) were marginal ($< 10\%$) at 1.0 μg mL^{-1}. Depressive effects from Bi, Se and Sn were not significant below 0.1 μg mL^{-1}. The method was validated by determination of Cd using ICP-MS in certified reference materials of Nearshore seawater (CASS-4), Bone ash (SRM 1400), Dogfish liver (DOLT-4) and Mussel tissue (SRM 2976).

1. Introduction

Cadmium is a toxic heavy metal that is released to the environment mainly from anthropogenic sources, including discharges from plating industry and smelters, power stations and waste batteries. It is an extremely toxic element that leads to hepato, renal and neurotoxicity even at low levels [1–3]. Over the last two decades, there has been a growing effort to develop sensitive methods for accurate determination of Cd as the regulatory agencies lower the permissible levels of this toxic element in environmental and nutritional samples.

Chemical vapor generation has been considered as an efficient sample introduction approach for determination of Cd by atomic spectroscopy techniques [4–21]. Based on the generation of volatile species of Cd (e.g., Cd^0 and CdH_2) through reactions with sodium borohydride ($NaBH_4$), vapor generation combines the advantages of matrix elimination and gaseous sample transport affording improved sensitivity and lower detection limits for direct analysis of complex samples. It has been used for determination of trace levels of Cd by FAAS [4,6,9,11,14–17], ETAAS [7,10,12,20], ICP-AES [18], ICP-MS [19–21] and atomic fluorescence spectrometry (AFS) [5,13]. More recently, electrochemical hydride generation (ECHG) has been reported for determination by AAS, where volatile Cd species are generated by the reactions of Cd(II) with hydrogen atoms that are produced electrochemically on the cathode surface [22–24].

Despite its inherent advantages in providing better selectivity and sensitivity for many hydride/vapor forming elements (e.g., As, Hg, Sb, and Se), vapor generation has not become as popular as other analytical approaches, such as coprecipitation and solid phase extraction for determination of Cd. Difficulties arise from a number of variables, such as poor efficiency, vapor instability and quenching or interferences in solution. It is well documented that the efficiency of Cd vapor generation is highly influenced by experimental settings and apparatus [4–24]. Transition metals and hydride forming elements, such as Cu(II), Fe(III), Ni(II), Pb(II) and Sn(II), have been reported to quench the efficiency regardless volatile Cd species are generated by chemical or electrochemical

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

0039-9140/$ - see front matter
http://dx.doi.org/10.1016/j.talanta.2013.06.039

approaches [4–24]. Numerous attempts have been made to alleviate the interferences of the transition metal ions by modifying the reaction medium with surfactants and adding masking agents and catalyst elements. Sanz-Medel and co-workers [20,25] reported that surfactants, specifically didodecyldimethylammonium bromide (DDAB) enhanced the sensitivity of vapor generation affording a detection of 80 ng L^{-1} with CV-AAS and 7 ng L^{-1} with ICP-MS. In contrast, Liva Garrido et al. [8] did not observe any improvement in the sensitivity in the presence of DDAB. The detection limits were somewhat similar, 0.15 and 0.05 ng L^{-1}, respectively, with and without DDAB for CV-AAS.

Among a number of masking agents, including thiourea, L-cysteine, cupferron, EDTA, tartaric acid, thiourea and L-cysteine enhanced the generation of Cd vapor in the presence of trace levels of Co(II) [4,5,9,12,14,19]. However, the performances of these masking agents in a medium kinetically catalyzed by Co(II) were not adequate to overcome severe suppression from Bi(III), Cu (II), Pb(II). Li et al. [13] proposed that sodium iodate ($NaIO_3$) as an additive also enhanced the generation of volatile Cd species in acidic medium. The authors explained the role of $NaIO_3$ with the formation of volatile cadmium halide (e.g., CdI_2) with iodide (I^-) produced from reduction of $NaIO_3$ by borohydride (e.g., KBH_4). The volatile CdI_2 were more stable than Cd^0 and CdH_2 resulting in improved transport of the vapor to the atomizer. Unfortunately, the method has not been applied to real samples nor is there any data related to the effects of the transition metals; therefore, the actual performance of $NaIO_3$ still remains to be verified.

The volatile species of Cd has been known to be very unstable, which is another obstacle on the poor efficiency of Cd vapor generation. Yet, an overview of the literature related to chemical approaches reveals that a great deal of problems occur in solution phase due to the quenching of the generation of gaseous Cd species (e.g., CdH_2) by certain transition metals [4–12]. Electrochemical vapor generation suffers from same interferences despite a different route of generation of the volatile species [23,24]. In a recent paper, we have utilized potassium hexacyanochromate(III) as a new additive for generation of Cd vapor and achieved an enhancement in sensitivity by more an order of magnitude in comparison to that achieved by conventional nebulization [26]. Equally important, the interferences from transition metals (Cu, Fe, Zn, and Ni) were alleviated affording accurate determination of Cd in different matrices.

In this paper, we report a novel reagent, cyanovanadate(III) complex, and a new methodology for determination of Cd by vapor generation approach. The heptacyanovanadate(III) complex was generated by reacting aqueous solutions of vanadium(III) chloride (VCl_3) and potassium cyanide (KCN) and then interacting the resulting $V(OH)_3$ suspension with acidic sample solution. Experimental conditions were optimized for a series of tasks from generation of the complex to affecting Cd vapor generation and to analysis of real samples by ICP-MS. Effects of transition metals and hydride forming elements were examined to compare the analytical performance of the cyanovanadate(III) complex with that of hexacyanochromate(III) in alleviating chemical interferences.

2. Experimental

2.1. Reagents and materials

Deionized water (18.2 MΩ cm resistivity) was used in all preparations. For vapor generation studies, a 1.0 μg mL^{-1} multielement stock solution hydride/vapor forming elements, including As, Bi, Cd, Hg, Pb, Sb, Se, Sn, Te in 1% v/v HCl was prepared from 1000 μg mL^{-1} standards (Spex Certiprep, Metuchen, NJ). Working solutions (10 μg L^{-1}) were prepared from this multielement solution to monitor the effect of the cynovanadate(III) complex on multielement system simultaneously. Vanadium (III) chloride (VCl_3, 97%, Lot No: 15996MMV), potassium cyanide (KCN, Bioultra ≥98%, Lot No: BCBG2070V) and sodium borohydride ($NaBH_4$, ≥98%, Lot No: 31396JJ) were purchased from Sigma Aldrich, St. Louis, MO. Vanadium (III) chloride and potassium cyanide solutions were prepared in water. Sodium borohydride solution was prepared daily in 0.1% m/v sodium hydroxide (NaOH) solution. For interferences studies, solutions of the test elements were prepared from high-purity salts for alkaline and alkaline earth elements (Ca, Mg, Na and K) and from 1000 μg mL^{-1} stock solutions of transition elements and hydride forming elements. Hydrogen peroxide (H_2O_2, 99.999%, Sigma Aldrich, Batch No: 09327LE) was used for digestion of samples. Solutions of VCl_3 and KCN were tested for elemental impurities. No significant Cd was detected in 0.1% m/v solutions. Both reagents were predicted to be ultrapure (i.e., 99.99%) for Cd. The HCl and HNO_3 solutions (BDH Chemicals) were of trace metal grade.

2.2. Instrumentation

Studies were conducted by using a Varian 820-MS ICP-MS instrument (Varian, Australia). The instrument was equipped with a peltier-cooled double-pass glass spray chamber serving as gas–liquid separator, quartz torch, and standard Ni sampler and skimmer cones. Prior to installation of vapor generation manifold, the instrument was tuned for mass calibration, sensitivity, doubly charged ions (< 2%) and oxides (< 3%) with 5 μg L^{-1} solution of ^{138}Ba, ^{25}Mg, ^{115}In, ^{140}Ce, ^{208}Pb. Samples were introduced manually. Data were acquired by ICP-MS Expert software package (version 2.2 b126). The operating parameters of the instrument and vapor generation conditions are summarized in Table 1.

Test solutions and calibration standards contained Sn that has isobaric overlaps on major isotopes of Cd, namely ^{112}Cd (24.13% abundant) and ^{114}Cd (28.73% abundant). Further, Sn forms hydride (SnH_4) more efficiently in a large acidity gradient to cause interferences by ^{112}Sn (0.97% abundant) and ^{114}Sn (0.65% abundant) on these isotopes of Cd [45 26]. To avoid the isobaric interferences from Sn on ^{112}Cd and ^{114}Cd isotopes, the less abundant isotopes ^{110}Cd (12.49% abundant) and ^{111}Cd (12.80% abundant) were used along all the experimental work. These isotopes of Cd are free from isobaric overlaps of Sn.

Table 1
Operating conditions for Varian 820-MS ICP-MS and vapor generation system.

ICP-MS		
RF Power (kW)		1.4
Plasma Ar flow (L min^{-1})		18
Auxiliary Ar flow (L min^{-1})		1.8
Nebulizer Ar flow (L min^{-1})		1.2
Sheath Ar flow (L min^{-1})		0.1
Sampling depth (mm)		7
Pump rate (mL min^{-1})		1.0
Stabilization time (s)		40
Spray chamber temperature (°C)		2
Scan mode		Peak hopping
Dwell time (ms)		0.05
Points/peak		1
Scans/peak		6
Scans/replicate		10
Isotopes measured		^{110}Cd and ^{111}Cd
Vapor generation		
Remark	Concentration	Flow rate (mL min^{-1})
Solution acidity	4% v/v HCl	1.0
VCl_3	0.04 mol L^{-1}	0.5
KCN	0.12 mol L^{-1}	0.5
$NaBH_4$	2% m/v	1.0

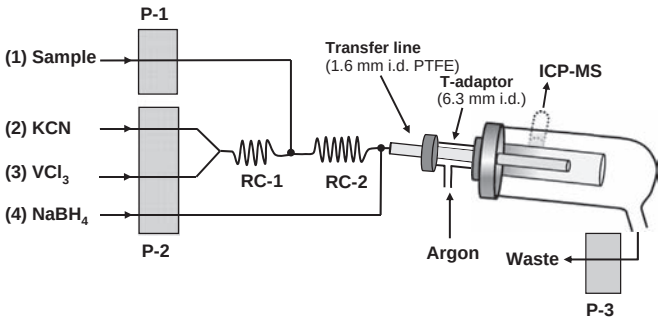

Fig. 1. Schematic diagram of the vapor generation manifold. A peltier-cooled double-pass glass spray chamber was used as gas–liquid separator (GLS). The transfer line was 15-cm long teflon tubing (1.6 mm i.d.). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Vapor generation setup

The schematic diagram of the vapor generation manifold is illustrated in Fig. 1. Double-pass glass spray chamber (100 mL inner volume) of the ICP-MS instrument was converted to gas–liquid separator as shown in Fig. 1 [26]. The stand-alone spray chamber is equipped with a push-fit teflon end-cap for nebulizer installation. The nebulizer was removed and a polypropylene T-adaptor (6.3 mm i.d.) was installed to the nebulizer housing of the teflon end-cap. A 15-cm long PTFE transfer tubing (1.6 mm. i.d., 1.8 mm o.d.) was inserted through the T-adaptor, which extended into the spray chamber when the teflon cap was installed on the spray chamber (Fig. 1). One end of the T-adaptor was connected to nebulizer gas port of ICP-MS instrument. The other end sleeving the transfer line was tightly sealed to prevent leak of argon gas. Three peristaltic pumps and tygon pump tubings were used to deliver the solutions. The pump tubings were red–red stop (1.14 mm i.d.) for sample and $NaBH_4$ solutions, black–black stop (0.76 mm i.d.) for VCl_3 and KCN, and purple–white stop (2.79 mm i.d.) for waste. The RC-1 and RC-2 reaction lines were made of 5- and 10-cm long tygon tubing (1.4 mm i.d.). Connections were made by using PTFE tubings (0.8 mm i.d.). Carrier gas flow was controlled by nebulizer argon introduced through the T-piece.

2.4. General procedure

Aqueous solutions of 0.04 mol L^{-1} VCl_3 and 0.12 mol L^{-1} KCN were mixed on-line at 0.5 mL min^{-1} and reacted through RC-1. This reaction yielded a suspension of $V(OH)_3$ in alkaline medium of KCN (pH 10.5–11). The suspension was injected and dissolved on-line in the acidic stream of sample solution in 4% v/v HCl along the RC2-line yielding the vanadium(III) cyanide complex, $[V(CN)_7]^{4-}$. The sample solution containing the complex was then reacted with 2% m/v $NaBH_4$ running at 1.0 mL min^{-1} to generate of volatile species of Cd. The vapor was swept through the peltier-cooled GLS and introduced to argon plasma of ICP-MS.

2.5. Sample preparation

Several certified reference materials (CRMs) were used for method validation. The samples were selected from mainly organic to predominantly inorganic matrices to test the performance of method under different conditions. The CRMs include Nearshore seawater (CASS-4) and Dogfish liver (DOLT-4) from the National Research Council Canada, and Bone ash (SRM 1400) and Mussel tissue (SRM 2976) from the National Institutes of Standards and Technology, Gaithersburg, MD. The seawater (CASS-4) samples were analyzed directly by adjusting the acidity of 10 mL of the bottled solution to 4% v/v HCl. Bone ash (SRM 1400) is purely calcium phosphate produced from calcinations of bone. Approximately, 50 mg sub-samples were digested in 1.0 mL concentrated HNO_3 in 4-mL PTFE tubes (Savillex) at 120 °C using Digiprep Cube digestion system (SCP Science, Champlain, NY). The solutions were first heated to dryness, and then redissolved with 1.0 mL water and reheated to dryness to remove traces of HNO_3. The final residue was dissolved and diluted to 10 mL with 4% v/v HCl.

The mussel tissue and dogfish liver are predominantly organic samples. For digestion, approximately, 50 mg sub-samples were digested with 2.0 mL concentrated HNO_3 and 1.0 mL H_2O_2 in 60-mL screw-capped PTFE tubes (Savillex) at 140 °C for 2 h. Additional 1.0 mL of H_2O_2 was added to hot samples at the completion of the first digestion cycle to destroy the organic material. The contents were evaporated to near dryness. Then the residue was dissolved in 2.0 mL water and reheated to dryness to remove excess HNO_3 and H_2O_2. This process was performed twice to completely eliminate residual H_2O_2 which interferes with generation of vanadium(III) cyanide complex. At the end of the second drying step, contents were dissolved in 4% v/v HCl and completed to 10 mL.

3. Results and discussion

3.1. Preliminary studies with V(III) cyanide complexes

The structure of cyanide complexes of V(III) is rather uncertain as it forms a variety of cyano-complexes. It was assumed to be hexacyanovanadate(III), $[V(CN)_6]^{3-}$ (wine-colored complex), but the synthesis of this complex was reported to be problematic since it could not be repeated by others for decades [27]. Conversely, single crystal X-ray data suggested that the complex that was thought to be $[V(CN)_6]^{3-}$ was infact $[V(CN)_7]^{4-}$ [27,28]. Additionally, the blue complex which was thought to be $[V(CN)_6]^{2-}$, was confirmed as $[VO(CN)_5]^{3-}$ from X-ray data [28]. In this study, we initially investigated the effects of cyanide complexes of vanadium(III) on Cd vapor generation with off-line approach in that the V(III) was complexed with CN^- by mixing stoichiometric amounts of the solid VCl_3 (dark violet crystalline solid) and KCN in 50-mL tubes according to the literature [27,28]. The dark crystalline powder was weighed and dissolved in dilute HCl (0.1% v/v) under a fume-hood. The color of the solution was green indicating the hydrated form of V(III), $[V(H_2O)_6]^{3+}$. An intense dark green–grey precipitate, viz. $V(OH)_3$, formed when KCN crystals were added. This mixture was stirred for about 10 min and then dissolved slowly by adding 10% v/v HCl. The color of the solution turned from turbid red to green and then to blue. The reddish solution was the most unstable turning to green in a few seconds. Green-colored solution was persistent even in slightly acidic medium. In excess of HCl (ca. 2–3% v/v), the color turned blue and remain unchanged, *viz*. the acidic form $[VO(H_2O)_5]^{2+}$.

It was assumed that cyanide complexes were $[V(CN)_7]^{4-}$ for green solution and $[VO(CN)_5]^{3-}$ in the blue solution. We performed vapor generation with both green and blue complexes. The improvement in Cd signals with both complexes was significant when acidic multielement standard solutions (10 μg L^{-1}) were mixed on-line with the complexes and then reacted with 2% m/v $NaBH_4$. The signals with $[V(CN)_7]^{4-}$ were slightly higher than those with $[VO(CN)_5]^{3-}$. More importantly, freshly prepared complexes performed better. The signals declined progressively as the solutions were exposed to air. Suspending particles developed within 2 to 3 h period in green-colored solution. Similar symptoms were also observed for hexacyanochromate(III) [26] and hexacyanomanganate(III) [29]. This was due to the instability of the cyanovanadate complexes when exposed to air. To overcome these difficulties,

the cyanide complex of vanadium(III) was produced in a flow system on-line and interacted with the sample solution as described in Fig. 1.

3.2. On-line formation of V(III) cyanide complex and its effect on Cd vapor generation

For on-line studies, both VCl_3 and KCN were dissolved in water. The aqueous solutions of VCl_3 were visually stable for about a week. Initially, V(III) and KCN solutions were prepared at 0.02 and 0.12 mol L^{-1}, respectively. The reaction of V(III) and KCN along the RC-1 line yielded a suspension that dissolved readily in the acidic stream and mixed with sample along the RC-2 line.

To determine the effects of reagents on Cd vapor generation, the acidity of the sample solutions (10 μg L^{-1} multi-element solution) was varied from 0 to 10% v/v HCl. In this experiment, lengths of the RC-1 and RC-2 were tentatively adjusted to 5 and 30 cm, respectively. The results are illustrated in Fig. 2 along with those obtained for individual solutions of 0.02 mol L^{-1} V(III) and 0.12 mol L^{-1} KCN solutions. In the absence of V(III) and KCN solutions, deionized water was pumped through lines (2) and (3) and mixed with 10 μg L^{-1} multielement solution followed by reaction with $NaBH_4$. In this case, generation of Cd vapor was negligible (see Water–water in Fig. 2). To test the effect of V(III), 0.02 mol L^{-1} V(III) solution was pumped via line (3) and was mixed with water running through line (2). For examining the effect of KCN, 0.12 mol L^{-1} KCN solution was pumped via line (2) and mixed with water from line (3). It is clear from Fig. 2 that V(III) solution did not have any effect alone, while signals were boosted to some extent when 0.12 mol L^{-1} KCN solution was mixed with the multielement solution. Cadmium signals, on the other hand, were increased significantly in the presence of cyanovanadate(III) complex. The enhancement was as high as 20-fold in comparison to that from nebulization of the same solutions. The highest signals were obtained between 3 and 5% v/v HCl range with an optimum at 4% v/v HCl. The working range was very broad for 0.12 mol L^{-1} KCN (e.g., KCN line) spanning from 2 to 6% v/v HCl due to the buffering of KCN-HCN medium. For V(III)–KCN medium, signals dropped sharply above 5% v/v HCl, which was attributed to reduced buffering capacity, viz. lower free CN^- in the medium since CN^- was complexed with V(III). Still though, the range from 3 to 5% v/v HCl was relatively wide to achieve stability in generation of Cd vapor.

It has been shown that cyanide complexes of certain first raw transition metals (e.g., Mn, Cr and Fe) facilitate formation of covalent hydrides of hydride forming elements [26,28–30]. While hexacyanochromate(III) complex has been effective in the generation of Cd vapor (CdH_2), hexacyanomanganate(III) and hexacyanoferrate(III) promote the generation of PbH_4 more effectively than any reagent reported to date [28–30]. The enhancement in Cd signals in V(III)–KCN medium pointed to the fact that cyanovanadate(III) complex, $[V(CN)_7]^{4-}$, infact facilitated the generation of volatile species of Cd upon reaction with $NaBH_4$. The actual mechanism underlying the action of the transition metal complexes on hydride formation is not fully understood yet. It was proposed that the reaction of transition metal cyanide complexes with $NaBH_4$ generates intermediate borane complex species that catalyze the formation of volatile covalent hydrides as they react with the particular metal ion [30]. In light of this information, the results suggest that reaction of cyanovanadate(III) complex with $NaBH_4$ yields reactive intermediates that enhance the generation of CdH_2.

3.3. Effects of V(III) and KCN concentrations on Cd vapor generation

The concentrations of the V(III) and KCN solutions were examined with univariate approach from 0 to 0.2 mol L^{-1} for each. As shown above, the KCN enhanced the signals even in the absence of V(III), therefore, its concentration was varied for 0.02 mol L^{-1} V(III). Then, the effect of V(III) concentration was investigated for optimum KCN condition. The results are shown in Fig. 3. Cadmium signals increased with increasing KCN concentration to about 0.04 mol L^{-1} and then remained relatively constant up to 0.2 mol L^{-1}. Although small concentration of KCN appeared to sufficient in the absence of interfering transition metals, higher concentration of KCN was better to achieve comparable signals between daily measurements. This effect was attributed to the better stabilization of the cyanovanadate(III)) complex in the presence of excess KCN. As a result, KCN concentration was adjusted to 0.1 mol L^{-1} for optimization V(III). When V(III) concentration was increased, maximum signals were obtained within a range from 0.02 to 0.08 mol L^{-1} V(III). In this case, 0.04 mol L^{-1} was chosen to be the optimum V(III) concentration. Interestingly, the signals declined above 0.1 mol L^{-1} V(III) where the reaction

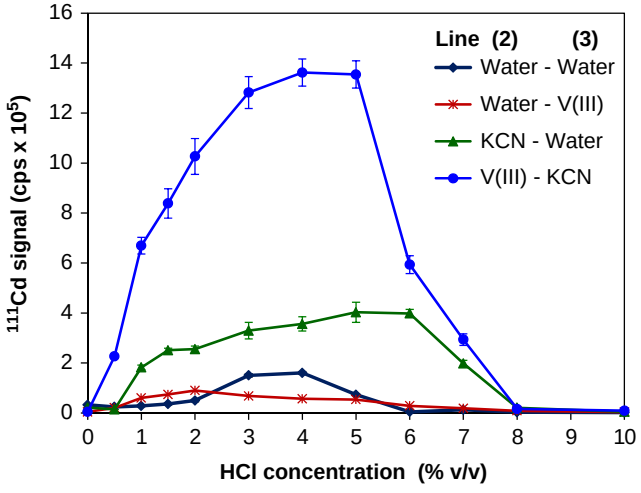

Fig. 2. Vapor generation profile for 10 μg L-1 Cd(II) solution along an acidity gradient from 0 to 10% v/v HCl using V(III), KCN and V(III)-KCN complex. V(III) = 0.02 mol L-1, KCN = 0.12 mol L-1; $NaBH_4$ = 2% m/v. The lengths of RC-1 and RC-2 were 5 and 30 cm, respectively. Line (2) and (3) in the legend indicates the solutions introduced via lines (2) and (3) on the manifold when examining the effects of individual reagents besides the V(III)-KCN medium.

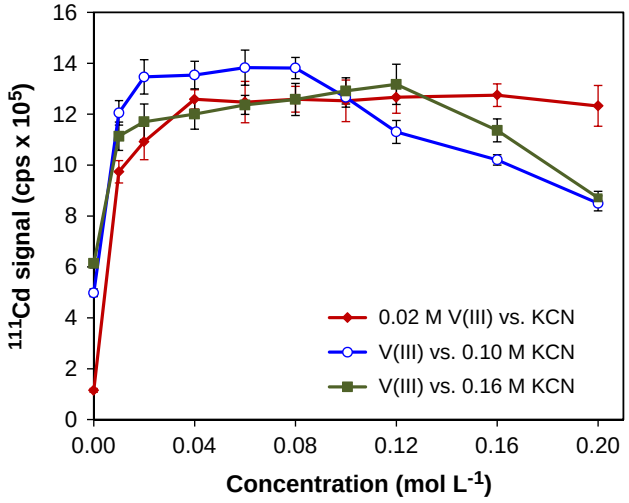

Fig. 3. The effects of V(III) and KCN concentrations on the vapor generation for 10 μg L-1 Cd(II) in multielement solution. Sample acidity = 4% HCl; $NaBH_4$ = 2% m/v, RC-1 = 5 cm; RC-2 = 30 cm.

medium contained elevated levels of free V(III) in relation to KCN. Additional studies conducted with 0.16 mol L^{-1} KCN showed that the depressive effects from excess V(III) could be tolerated to some extent, viz., more V(III) was complexed with KCN (see Fig. 3). The implications of this result were two-fold: (a) the cyanovanadate (III) complex plays a key role in vapor generation, and (b) excess of KCN at least 2 to 3-fold of V(III) provides better stability and reduces the interferences from excess V(III) and other matrix components. Based on these observations, V(III) and KCN concentrations were adjusted to 0.04 and 0.12 mol L^{-1}, respectively.

3.4. Optimization of manifold parameters

The major manifold parameters that influenced the vapor generation efficiency were the lengths of the reaction lines, flow rates of samples and nebulizer argon, and the concentration of $NaBH_4$. As mentioned in Section 3.1, mixing of VCl_3 and KCN yields $V(OH)_3$ precipitate. The length of RC-1 line affected the reaction time for the formation of $V(OH)_3$ suspension while that of RC-2 determined the dissolution of $V(OH)_3$ and formation of cyanide complex. The length of RC-1 was increased from 2 to 20 cm while that of RC-2 was examined between 5 and 30 cm for 1.4 mm i.d. tygon tubing For RC-1, 5-cm tubing was optimum (Fig. 4a). Signals declined significantly when RC-1 was longer than 10 cm. Moreover, significant deposition was noted along the walls of the RC-1 tubing. Thus, the declining signals were attributed to the loss of V (III) due to increased precipitation, namely, deposition of $V(OH)_3$ suspension on the walls of the tubing. Alternatively, incomplete dissolution of the $V(OH)_3$ in the acid stream was also thought to be responsible for the declining signals since $V(OH)_3$ would precipitate strongly along a longer RC-1. In case of RC-2, the signals declined to some extent with increasing tubing length to 30 cm, suggesting that 5- to 10-cm long tubing was suitable (Fig. 4a).

The effects of flow rates of sample solution and nebulizer argon gas are illustrated in Fig. 4b and c, respectively. The highest flow rate for sample solution was about 1.5 mL min^{-1}. Signals declined with increasing flow rates progressively. This behavior was consistent with that observed for the longer RC-1 lines, viz. $V(OH)_3$ did not dissolve completely when mixing with acidic solution along the 10-cm long RC-2 to form cyanovanadate(III) complex line. Therefore, flow rate of the sample solution was kept constant at 1.0 mL min^{-1}. The optimum flow rate for the nebulizer argon gas was 1.2 L min^{-1} when it was varied from 0.8 to 1.4 L min^{-1}. Sodium borohydride concentration was investigated from 0.5 to 3.5% m/v to determine the optimum level for Cd vapor generation. A concentration of 2% m/v $NaBH_4$ solution was sufficient to obtain maximum signals (Fig. 4d) that could be related with the operation of the vapor generation system at relatively low flow rates.

3.5. Effects of transition metals and hydride forming elements

It has been known that Cd vapor generation suffers from the interferences of transition metals (e.g., Cu and Ni) and hydride forming elements (Bi, Pb and Se) [4–25]. Thus, the effects of a number of common transition metals (Co, Cu, Fe, Mn, Ni and Zn) and hydride forming elements (As, Bi, Pb, Sb, Se and Sn) were investigated for 10 μg L^{-1} Cd(II) solutions under optimum conditions (e.g., 4% v/v HCl, 0.04 mol L^{-1} V(III), 0.12 mol L^{-1} KCN and 2% m/v $NaBH_4$). Relative signals obtained in the presence of the matrix elements are summarized in Table 2 and the performance of the method against chemical interference is compared in Table 3 with vapor generation procedures reported for Cd previously. It is clear from Table 3 that Cu(II), Ni(II) and Pb(II) are the severely interfering elements in Cd vapor generation in HCl-Co(II)-thiourea or HCl-Ni(II)-thiourea medium [5,9,12,19]. Additionally, As(III), Cr(VI) and Fe(III) induced significant suppression at 0.1 μg mL^{-1} levels in HNO_3 medium [12]. In this

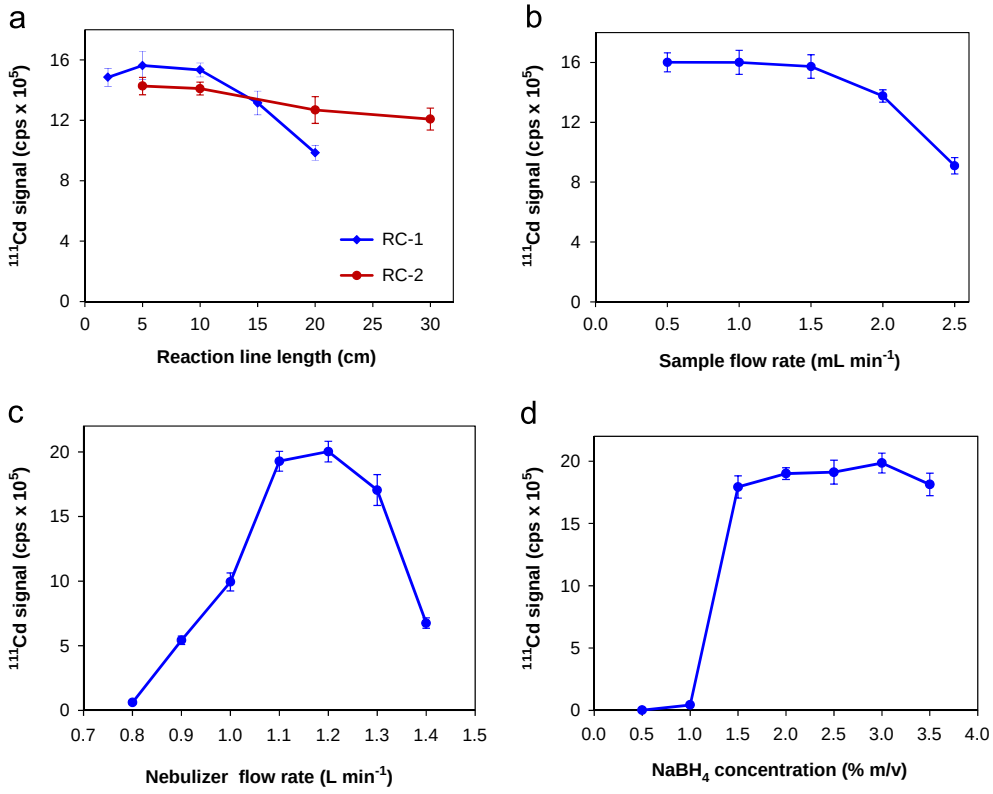

Fig. 4. Effects of various experimental parameters on Cd vapor generation for 10 μg L^{-1} Cd(II) in 4% v/v HCl in the presence of cyanovanadate(III) complex: (a) lengths of RC-1 and RC-2 lines; (b) sample solution flow rate; (c) nebulizer flow rate; (d) $NaBH_4$ concentration.

study, no significant interferences were observed from Fe(III), Mn(II) and Zn(II). Responses varied between 94 and to 103% when concentrations of the matrix elements ranged from 0.1 to 1.0 μg mL^{-1}. An enhancement was noted for 1.0 μg mL^{-1} Co(II). This element had also shown similar effects with different ligands, such as thiourea [5,9,10,12]. Copper is presumably the most depressing element along with Ni(II) on ;Cd vapor generation. Guo and Guo [5] utilized KCN to alleviate the interference from 0.05 μg mL^{-1} Cu(II) in HCl-Co(II)-thiourea medium. The results for Cu(II) and Ni(II) in the presence cyanovanadate(III) also indicate depressive effects from these severely interfering elements. However, the overall suppression was less than 10% even at 1.0 μg mL^{-1} levels. Similar performance was observed in the presence of hexacyanochromate(III) complex [26], indicating that transition metal cyanide complexes alleviate the interferences of Cu(II) and Ni(II) effectively.

Among the hydride forming elements, As(III) and Sb(III) had no suppressive effects on vapor generation. The latter was found to cause interferences in hexacyanochromate(III) medium (ca. 27 and 36% depression at 0.2 and 0.5 μg mL^{-1} levels, respectively) [26]. Suppression was also noted from Bi(III), Se(IV) and Sn(II) as reported in other studies [5,9,10,12]. However, the effects of these elements were alleviated at 0.1 μg mL^{-1} levels. Furthermore, the cyanovanadate(III) complex appeared to be more tolerant than hexacyanochromate(III) to the effects of Bi(III) and Sn(II) affording higher recoveries in the presence of 0.1 μg mL^{-1} Bi(III) and Sn(II) (see Table 2). Pb(II) induced some suppression at a concentration of 0.5 μg mL^{-1} (ca. 11% suppression). At the same Pb(II) concentration, the suppression was more pronounced in hexacyanochromate(III) medium (ca. 50% depression) [26]. This result also demonstrated that cyanovanadate(III) medium was advantageous in alleviating the depressive effects of Pb(II).. The effects of alkali and alkaline earth elements (Na, K, Ca and Mg) were also examined similarly. No significant interferences occurred from these elements at as high as 1000 μg mL^{-1} levels. Relative signals varied between were 95% for Mg to 106% for Na.

Table 2
Effects of transition metals and hydride forming elements on Cd vapor generation.

Matrix element	Concentration (μg mL^{-1})	Relative signal (%)
As(III)	0.1	98 ± 3
	0.5	99 ± 5
Bi(III)	0.1	88 ± 5
	0.5	73 ± 2
Co(II)	0.1	98 ± 3
	1.0	116 ± 6
Cu(II)	0.1	98 ± 2
	1.0	92 ± 4
Fe(III)	0.1	96 ± 5
	1.0	94 ± 3
Mn(II)	0.1	96 ± 3
	1.0	103 ± 3
Ni(II)	0.1	103 ± 2
	1.0	95 ± 6
Pb(II)	0.1	94 ± 3
	0.5	89 ± 4
Sb(III)	0.1	94 ± 5
	0.5	92 ± 3
Se(IV)	0.1	95 ± 4
	0.5	73 ± 3
Sn(II)	0.1	93 ± 2
	0.5	84 ± 4
Zn(II)	0.1	102 ± 3
	1.0	103 ± 2

3.6. Analytical figures of merit

Calibration was performed using aqueous multi-element standard solutions (As, Bi, Cd, Hg, Pb, Sb, Se, Sn, Te) that ranged from 0 to 2.0 μg L^{-1} in 4% v/v HCl. The calibration curve was linear within 0 to 2.0 μg L^{-1} (r^2=0.994–0.999). The method detection limits were calculated with 3 s rule (i.e., analyte concentration equivalent to 3 times the standard deviation of blank signal) for 4% v/v HCl solutions (n=13). Under the optimum conditions (e.g., 4% v/v HCl, 0.04 mol L^{-1} V(III), 0.12 mol L^{-1} KCN and 2% m/v $NaBH_4$), the background signals for the blank solutions ranged from 920 to 1200 cps that afforded a limit of detection (LOD) of 5.0 and 4.5 ng L^{-1} for ^{110}Cd and ^{111}Cd isotopes, respectively. Precision (%RSD) for was better than 4.7% for six replicate scans of standard solutions (0.02 to 2 μg L^{-1}). The sensitivity was improved by about 20-fold based on the ratio of calibration slopes of this method and solution nebulization for ^{110}Cd and ^{111}Cd isotopes. Water, dilute HNO_3 and HCl solutions were used for cleaning the manifold during replicate runs of 10 μg L^{-1} Cd solutions. Flushing the sampling lines with 4% v/v HCl for about 20 s at 4 mL min^{-1} was sufficient to successfully washout the manifold.

3.7. Method validation

A Neashore seawater (CASS-4) and bone ash (SRM 1400) certified reference samples were analyzed for validating the analytical performance of the method under saline matrices. The seawater contains about 3% m/v salt matrix made up of chlorides and sulfates of Na, K, Ca and Mg. The SRM 1400 is predominantly Ca (38.18%), P (17.91%) and Mg (0.684%). Other matrix components include Al (530 μg g^{-1}), Fe (660 μg g^{-1}), F (1250 μg g^{-1}), Pb (9.0 μg g^{-1}), Sr (249 μg g^{-1}) and Zn (181 μg g^{-1}). Sub-samples of CASS-4 were acidified to 4% v/v HCl. SRM 1400 were digested in HNO_3 which was completely evaporated before diluting the

Table 3
Comparison of the performances of vapor generation (VG) procedures reported for determination Cd.

Technique	Medium	Interfering ions at 0.1 μg mL^{-1}	LOD (ng L^{-1})	Reference #
ICP-MS	HCl-V(III)-KCN-$NaBH_4$	Bi(III)	0.0045	This work
ICP-MS	HCl-Cr(III)-KCN-$NaBH_4$	Bi(III) and Sn(II)	0.0057	[26]
AFS	HCl-Co(II)-Thiourea-KBH_4	Cu(II), Pb(II)	0.008	[5]
AAS	HCl-DDAB-$NaBH_4$	Not reported	0.15	[8]
AAS	HCl-Ni(II)-Thiourea-$NaBH_4$	Ag(I), Cu(II), Ni(II), Pb(II)	0.016	[9]
AFS	HCl-$NaIO_3$-KBH_4	Not reported	0.010	[13]
ETAAS[a]	HNO_3-Co(II)-Thiourea-$NaBH_4$	As(III), Cu(II), Cr(VI), Pb(II), Fe(III)	0.004	[12]
AAS[b]	HCl-$NaBH_4$	Cu(II)	0.56	[15]
ID-ICPMS	HCl-Co(II)-Thiourea-$NaBH_4$	Cu(II), Ni(II), Pb(II)	0.026	[19]
FI-ICPMS	HCl-DDAB-$NaBH_4$	Not reported	0.007	[20]
ECHG-AAS	NaCl and phosphate buffer (pH 7.0)	Not reported	0.61	[24]

[a] Via *In Situ* preconcentration.
[b] Via cloud point extraction/preconcentration.

Table 4
The results for Cd determined in different certified reference materials by vapor generation ICP-MS. Results are given as mean ± standard deviation of five replicate analyses for each sample. Values in parenthesis are "information only".

Sample	Isotope	Found	Certified value
Nearshore seawater (CASS-4) ($\mu g\ L^{-1}$)	^{110}Cd	0.026 ± 0.002	0.026 ± 0.003
	^{111}Cd	0.029 ± 0.002	
Bone ash (SRM 1400) ($\mu g\ g^{-1}$)	^{110}Cd	0.031 ± 0.004	(0.03)
	^{111}Cd	0.030 ± 0.004	
Dogfish liver (DOLT-4) ($\mu g\ g^{-1}$)	^{110}Cd	24.4 ± 0.7	24.3 ± 0.8
	^{111}Cd	24.5 ± 0.7	
Mussel tissue (SRM 2976) ($\mu g\ g^{-1}$)	^{110}Cd	0.74 ± 0.03	0.82 ± 0.16
	^{111}Cd	0.75 ± 0.04	

digests to 10 mL with 4% v/v HCl for analysis (see Section 2.5). The results are summarized in Table 4 for ^{110}Cd and ^{111}Cd isotopes. The values for Cd from these samples were consistent with the certified and indicative values. No significant differences were noted at 95% confidence level. The results for bone ash were also significant as to validate the tolerance of the procedure to high concentrations of aluminum, phosphates and fluoride.

In contrast to seawater and bone ash, dogfish liver (DOLT-4) and mussel tissue (SRM 2976) are composed of largely organic material. The digestion of these samples was therefore performed in the presence of H_2O_2 with HNO_3. In a previous study involving the hexacyanochromate(III) for Cd vapor generation [26], it was found that the transition metal cyanide complexes were highly susceptible to traces of H_2O_2. This phenomenon was ascribed to the rapid decomposition of the complex in an oxidizing medium before interacting with $NaBH_4$. Consequently, it was very critical to remove residual H_2O_2 from the digest by repetitive heating as described in Section 2.5. In addition, appropriate volumes of stock solutions were diluted 10-fold and 100-fold for SRM 2976 and DOLT-4, respectively, to bring Cd levels within the range of calibration. The results for SRM 2976 and DOLT-4 following such treatments agreed with the certified values within 95% confidence level (Table 4).

4. Conclusion

The results presented in this paper demonstrate that cyanovanadate(III) complex possesses unique chemical properties for generation of volatile species of Cd. Until recently, hexacyanoferrate(III) was the only reagent affecting the generation of PbH_4. The results for cyanovanadate(III) along with those for hexacyanochromate(III) [26] and hexacyanomanganate(III) [29] indicate that the transition metal cyanide complexes act selectively on hydride forming elements. This selectivity is assumed to be related with the intermediate species that are mediated by the chemical and catalytic properties of the metal ion (e.g., Cr, Fe, Mn and V). In other words, different borane intermediates are produced for different cyanide complexes of transition metals that catalyze generation of volatile hydrides of different elements [26,29–31].

This report is the first to utilize a combination of V(III) and KCN for determination Cd by vapor generation in real samples. Previous attempts for generation of Cd vapor for analytical purposes have mostly concerned a number of oxidizing and complexing agents, but were far from overcoming the interferences of transition elements. In contrast, the procedure developed in this study is not affected from the presence of common transition metals (e.g., Co, Cu, Fe, Mn, Ni and Zn) and some common hydride forming elements (As, Pb and Sb) at $\mu g\ mL^{-1}$ (ppm) levels. The effects of other hydride forming elements (Bi, Se, and Sn) are not expected to pose any limitation to the analytical performance of the method since these elements are often present at $\mu g\ L^{-1}$ to $ng\ L^{-1}$ levels in most samples. Evidently, hydride forming elements, including Bi, Pb, Sb and Sn, exhibited significant suppression on Cd vapor generation in the previous report involving the hexacyanochromate(III) complex [26]. In comparison to that, this procedure was more tolerant to higher concentrations of Bi(III), Pb(II) and Sn(II), while the interferences from Sb(III) were readily alleviated at up to 0.5 $\mu g\ mL^{-1}$ Sb levels.

Acknowledgements

This project was supported by grants from the National Center for Research Resources (5 G12 RR013459-15), the National Institute on Minority Health and Health Disparities (8 G12 MD007581-15) and the Research Initiative for Scientific Enhancement (2 R25 GM067122) from the National Institutes of Health. The views expressed herein are those of 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 Turkish Higher Education Council (YOK) to Dr. Vedat Yilmaz during his stay at Jackson State University.

References

[1] C.D. Klaassen, J. Liu, Drug Metab. Rev. 29 (1997) 79.
[2] M. Shibutani, K. Mitsumori, N. Niho, S. Satoh, H. Hiratsuka, M. Satoh, M. Sumiyoshi, M. Nishijima, Y. Katsuki, J. Suzuki, J. Nakagawa, M. Ando, Arch. Toxicol. 74 (2000) 571.
[3] L. Chen, L. Lei, T. Jin, M. Nordberg, G.F. Nordberg, Diabetes Care 29 (2006) 2682.
[4] X.-W. Guo, X.-M. Guo, J. Anal. At. Spectrom. 10 (1995) 987.
[5] X. Guo, X. Guo, Anal. Chim. Acta 310 (1995) 377.
[6] M. Liu, S. Xu, At. Spectrosc. 18 (1997) 195.
[7] H. Matusiewicz, M. Kopras, R.E. Sturgeon, Analyst 122 (1997) 331.
[8] M. Liva Garrido, R. Munoz-Olivas, C. Camara, J. Anal. At. Spectrom. 13 (1998) 295.
[9] C. Vargas-Razo, J.F. Tyson, Fresenius J. Anal. Chem. 366 (2000) 182.
[10] L. Lampugnani, C. Salvetti, D.L. Tsalev, Talanta 61 (2003) 683.
[11] Y.-L. Feng, R.E. Sturgeon, J.W. Lam, Anal. Chem. 75 (2003) 635.
[12] W. Chuachuad, J.F. Tyson, Can. J. Anal. Sci. Spectros. 49 (2004) 362.
[13] G. Li, L. Wu, J. Xin, X. Hou, J. Anal. At. Spectrom. 19 (2004) 1010.
[14] W. Chuachuad, J.F. Tyson, J. Anal. At. Spectrom. 20 (2005) 273.
[15] J.L. Manzoori, H. Abdolmohammad-Zadeh, M. Amjadi, Talanta 71 (2007) 582.
[16] N. Pourreza, K. Ghanem, J. Hazard. Mater. 78 (2010) 566.
[17] S. Sahan, U. Sahin, Talanta 88 (2012) 701.
[18] M.C. Valdes-Hevia y Temprano, M.R. Fernandez de la Campa, A. Sanz-Medel, J. Anal. At. Spectrom. 9 (1994) 231.
[19] T.-J. Hwang, S.-J. Jiang, J. Anal. At. Spectrom. 12 (1997) 579.
[20] H.G. Infante, M.L.F. Sanchez, A. Sanz-Medel, J. Anal. At. Spectrom. 13 (1998) 899.
[21] Y.-T. Chang, S.-J. Jiang, J. Anal. At. Spectrom. 23 (2008) 140.
[22] M.H. Arbab-Zavar, M. Chamsaz, A. Youssefi, M. Aliakbari, Anal. Chim. Acta 546 (2005) 126.
[23] M.H. Arbab-Zavar, M. Chamsaz, A. Youssefi, M. Aliakbari, Talanta 97 (2012) 229.
[24] M.H. Arbab-Zavar, M. Chamsaz, A. Youssefi, M. Aliakbari, Microchem. J. 108 (2013) 188.
[25] A. Sanz-Medel, M.C. Valdes-Hevia y Temprano, N. Bordel Garcia, M.R. Fernandez de la Campa, Anal. Chem. 67 (1995) 2216.
[26] V. Yilmaz, L. Rose, Z. Arslan, M.D. Little, J. Anal. At. Spectrom. 27 (2012) 1895.
[27] B.M. Chadwick, A.G. Sharpe, in: H.J. Emeleus, A.G. Sharpe (Eds.), Advances in Inorganic Chemistry and Radiochemistry, Vol. 8, Academic Press, New York, 1966, pp. 92–93.
[28] S. Jagner, Acta Chem. Scand. Ser A 29 (1975) 255.
[29] V. Yilmaz, Z. Arslan, L. Rose, Anal. Chim. Acta 761 (2013) 18.
[30] A. D'Ulivo, M. Onor, R. Spiniello, E. Pitzalis, Spectrochim. Acta, Part B 63 (2008) 835.
[31] D. Afonso, Z. Arslan, S. Baytak, J. Anal. At. Spectrom. 25 (2010) 726.