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Search for new metal ion additives for improved cadmium vapor generation

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NEMC 2021

August 2-12, 2021 Bellevue WA

U.S. Department of the Interior
U.S. Geological Survey

Cadmium in the environment

- Cadmium (Cd) is a toxic metal & has no known biological utility
- Industrialization has increased exposure risks to Cd
- Cadmium accumulates primarily in the liver and kidney
- Half-life of Cd in the kidney is between 6 to 20 years
- Chronic exposure leads to nephrotoxicity and kidney failure
- Permissible exposure limits are very low

  5 µg/L (ppb) in drinking water (USEPA) & 15 mg/kg in food (FDA)

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Chemical vapor generation (CVG) for Cd detection

- Volatile species of Cd (CdH_2 and/or Cd vapor) can be produced when Cd(II) is reacted with sodium borohydride ($NaBH_4$).
- Generation of volatile Cd species is a difficult task because of the interferences of hydride forming elements (Pb and Se) and transition metal ions (Cu and Ni).
- The efficiency of Cd CVG is poor and highly dependent on experimental settings.

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CVG for ICP-MS

- **ICP-MS offers high sensitivity, precision and speed compared to atomic absorption and emission techniques**
- **However, ICP-MS is not suitable for complex samples**
- **Total dissolved solids (TDS) content must be less 0.2%**
  - Vapor generation allows volatile Cd species to be selectively produced and introduced to ICP-MS instrument.
  - Vapor generation improves detection capabilities of ICP-MS for direct analysis of complex samples.
  - Compared to 2-5% efficiency for nebulization, vapor generation affords about 80 to 100% efficiency in sample introduction.

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Cadmium - a problematic element in CVG

Cadmium vapor generation is a difficult task:

- poor generation efficiency for volatile Cd species
- strong dependency of vapor generation to chemical conditions (pH, catalytic/complexing agents and reductants)
- vulnerability of Cd vapor generation to interferences of transition metals present in sample

There is a need to overcome chemical interferences from transition metals!

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Progress in CVG for Cd determination

Cd CVG has been researched for 30 years, there is still no uniquely efficient chemical approach.

- Sanz-Medel et al. first generated Cd vapor using didodecyldimethylammonium bromide (DDAB) for FAAS (LOD 80 ng L^{-1}) *Sanz-Medel et al. , Anal. Chem., 1995,**67**, 2216.*
- Later extended this method to FI-HG-ICP-MS (LOD = 7 ng L^{-1}) *Infante et al., JAAS, 1998, **13**, 899.*
- A mixture of thiourea and Co(II) used first to enhance sensitivity. But severe interferences from **Au(III), Cu(II), Bi(III), Ni(II) and Pb(II).** *Guo and Guo, Anal. Chim. Acta, 1995, **310**, 377. Li et al. JAAS, 2011,**26**, 1488-1493.*
- Sodium iodate ($NaIO_3$) improved sensitivity 10-fold in acidic solutions, but interferences were not studied. *Li et al. JAAS, 2004, **19**, 1010.*

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Literature: Recent developments on Cd CVG

JAAS Dynamic Article Links

Cite this: *J. Anal. At. Spectrom.*, 2012, **27**, 1895

www.rsc.org/jaas **PAPER**

On-line chemical vapour generation of cadmium in the presence of hexacyanochromate(III) for determination by inductively coupled plasma mass spectrometry (ICP-MS)

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Received 2nd July 2012, Accepted 31st August 2012
DOI: 10.1039/c2ja30195d

A vapour generation (VG) procedure has been described for determination of Cd by ICP-MS. Volatile species of Cd were generated on-line by interacting acidic sample solution containing potassium hexacyanochromate(III), $K_3Cr(CN)_6$, with sodium borohydride ($NaBH_4$). The hexacyanochromate(III) complex was generated on-line by reacting 0.04 mol L^{-1} chromium(III) nitrate and 0.16 mol L^{-1} potassium cyanide (KCN) solutions in water. The resulting suspension of chromium(III) hydroxide, $Cr(OH)_3$, was fed continuously to acidic stream of sample solution in the presence of excess KCN. The experimental conditions were optimized for effective generation of volatile species of Cd. Optimum signals were obtained from reaction of sample solutions in 4% v/v HCl with 2% m/v $NaBH_4$ solution. The presence of $K_3Cr(CN)_6$ improved the efficiency of Cd vapour generation substantially affording 15-fold higher sensitivity. This phenomenon was thought to occur through formation of reactive intermediates evolved from the interaction of $[Cr(CN)_6]^{3-}$ with $NaBH_4$ that react with Cd(II) to increase the yield of volatile Cd species. Under the optimum conditions, no significant interferences were observed from the transition metals, including Cu and Ni, up to 1.0 µg mL^{-1} levels. Among the hydride forming elements, Bi, Pb, Sb and Sn depressed the signals above 0.1 µg mL^{-1}. The detection limits (3 s) were 6.2 and 5.2 ng L^{-1} for ^{110}Cd and ^{111}Cd isotopes, respectively. The method was successfully applied for determination of Cd by ICP-MS in several certified reference materials, including Nearshore seawater (CASS-4), Bone ash (SRM 1400), Dogfish liver (DOLT-4) and Mussel tissue (SRM 2976).

Talanta 115 (2013) 681–687

Contents lists available at SciVerse ScienceDirect

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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)

CrossMark

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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).

Literature: Recent developments on Cd CVG

Microchemical Journal 123 (2015) 170–178

Contents lists available at ScienceDirect

Microchemical Journal

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

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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)☆

CrossMark

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A R T I C L E I N F O

Article history:
Received 4 June 2015
Received in revised form 10 June 2015
Accepted 20 June 2015
Available online 26 June 2015

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

A B S T R A C T

In this study, a highly efficient chemical vapor generation (CVG) approach is reported for determination of cadmium (Cd). Titanium (III) and titanium (IV) were investigated for the first time as catalytic additives along with thiourea, L-cysteine and potassium cyanide (KCN) for generation of volatile Cd species. Both Ti(III) and Ti(IV) provided the highest enhancement with KCN. The improvement with thiourea was marginal (ca. 2-fold), while L-cysteine enhanced signal slightly only with Ti(III) in H_2SO_4. Optimum CVG conditions were 4% (*v*/*v*) HCl + 0.03 M Ti(III) + 0.16 M KCN and 2% (*v*/*v*) HNO_3 + 0.03 M Ti(IV) + 0.16 M KCN with a 3% (*m*/*v*) $NaBH_4$ 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 $NaBH_4$ 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).

Analytica Chimica Acta 1168 (2021) 338601

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

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Effect of additives on cadmium chemical vapor generation and reliable quantification of generation efficiency

Check for updates

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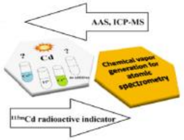
H I G H L I G H T S

- Chemical vapor generation (CVG) of Cd was investigated in a comprehensive way.
- Additive effects (Ti^{4+}/KCN; Cr^{3+}/KCN and Co^{2+}/ascorbic acid/thiourea) were studied.
- Cd CVG efficiency was low and irreproducible (3–15%) without any additives.
- Cr^{3+}/KCN and Ti^{4+}/KCN as additives improved Cd generation efficiency up to 70%.
- LOD of 60 pg mL^{-1} Cd was reached with Cr^{3+}/KCN additive and QTA-AAS detection.

G R A P H I C A L A B S T R A C T



A R T I C L E I N F O

Article history:
Received 14 March 2021
Received in revised form
23 April 2021
Accepted 29 April 2021
Available online 3 May 2021

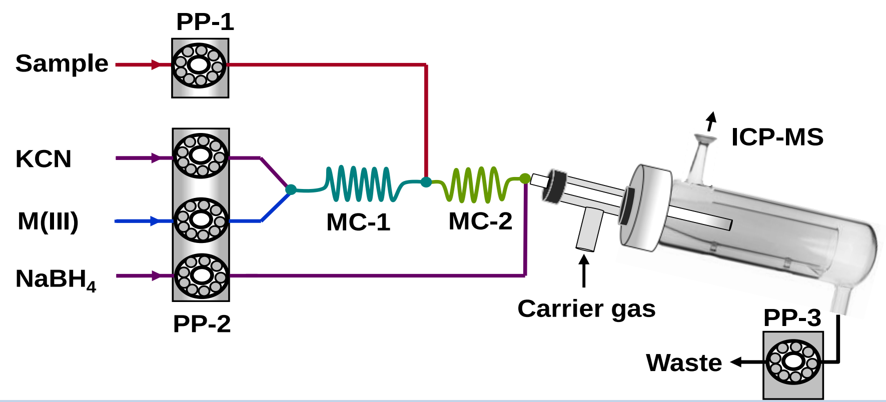
Keywords:
Chemical vapor generation
Cadmium
Atomic spectrometry
Generation efficiency
Radioactive indicator

A B S T R A C T

Chemical vapor generation (CVG) of cadmium was optimized based on response from atomic absorption spectrometry (AAS) with a heated quartz tube atomizer (QTA). Effect of several modifiers on analytical performance was studied. These additives were: inorganic salts of Cr^{3+}, Ti^{4+} and Co^{2+} and their on-line synthesized complexes with KCN and thiourea, respectively. The use of these additives resulted in sensitivity enhancement, better repeatability and correspondingly in improvement of overall CVG efficiency. The latter was quantified by two independent approaches: a) by means of ^{115m}Cd radioactive indicator, b) from comparison of sensitivities obtained with conventional solution nebulization and with CVG, both coupled simultaneously to inductively coupled plasma mass spectrometry. Both approaches provided comparable results. The highest efficiency, between 60 and 70%, was reached in the presence of Cr^{3+}/KCN and Ti^{4+}/KCN while 19% was achieved in Co^{2+}/ascorbic acid/thiourea environment. Highly irreproducible results with low CVG efficiency ranging from 2.5 to 15% were reached in the absence of any additives. The generated cadmium species were identified to be mostly free atoms regardless of the additives presence or their absence. Cr^{3+}/KCN environment was selected as the most robust for CVG of Cd reaching sensitivity of 6.6 s ng^{-1} Cd and limit of detection of 60 pg mL^{-1} Cd (9 pg Cd absolute) with detection by QTA-AAS.

Aim and instrumentation

The **aim of this study** was to investigate the effects of trivalent ions, including **aluminum, Al(III), scandium, Sc(III), and yttrium, Y(III),** on the generation of volatile Cd species and to develop a CVG method for determination of Cd by ICP-MS.



Varian 820-MS
ICP-MS

Schematic diagram of the CVG manifold. Glass spray chamber was used for gas-liquid separation.

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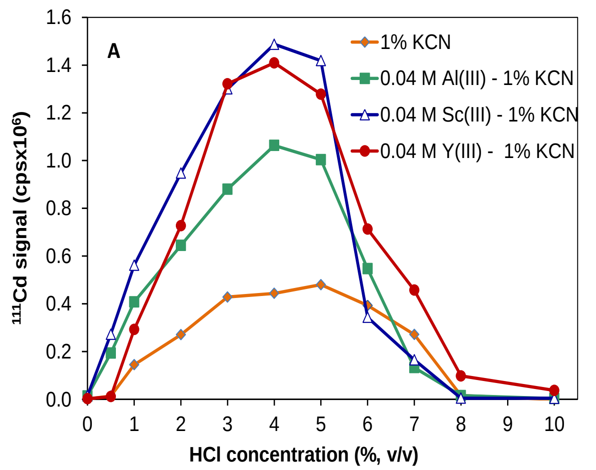
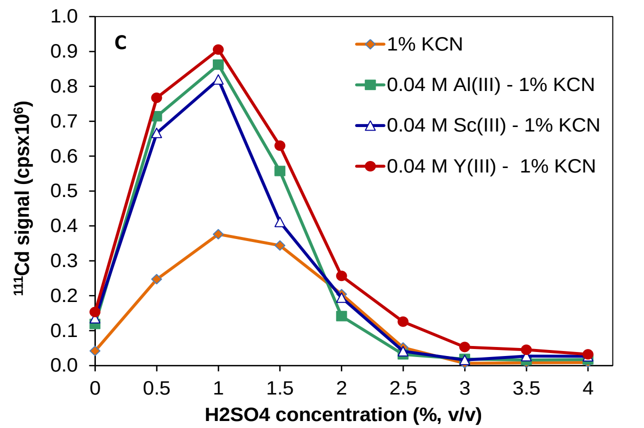
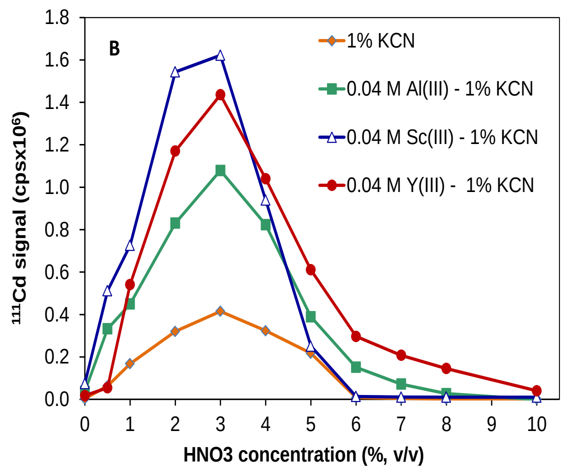
Preliminary examination of Cd CVG with Al(III), Sc(III), and Y(III)



HCl-M(III) vs CVG



H_2SO_4 – M(III) vs CVG



HNO_3 – M(III) vs CVG

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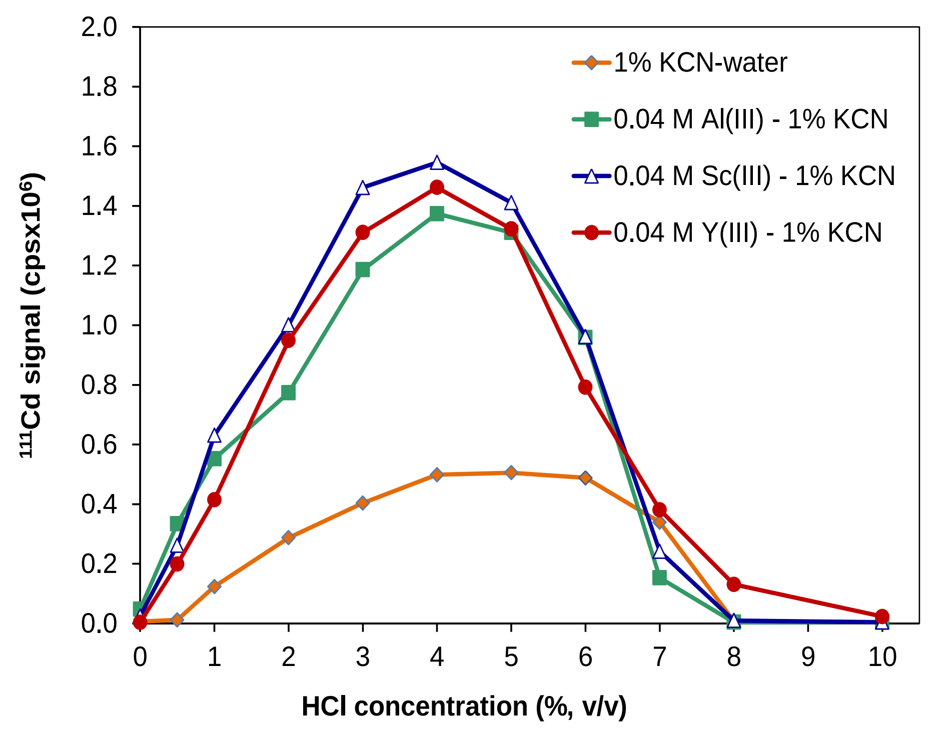
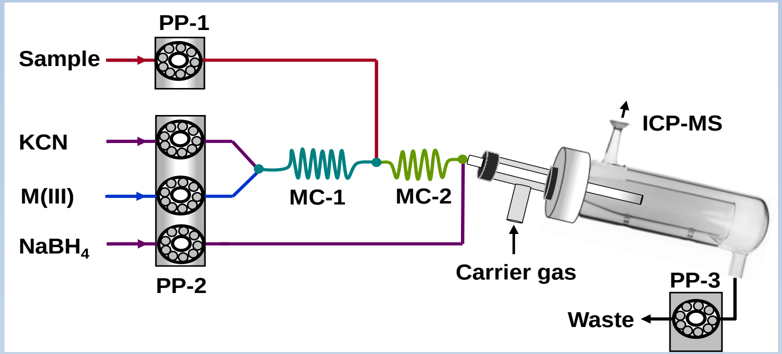
Optimum acid and its range for Cd CVG



CVG signal profiles for 10 µg L^{-1} Cd(II) as function of HCl concentration with Al(III), Sc(III) or Y(III) mixed on-line with KCN as complexing ligand. Water was run through M(III) channel for 1% KCN run. $NaBH_4$ = 2% (m/v), MC-1 = 5 cm; MC-2 = 15 cm.



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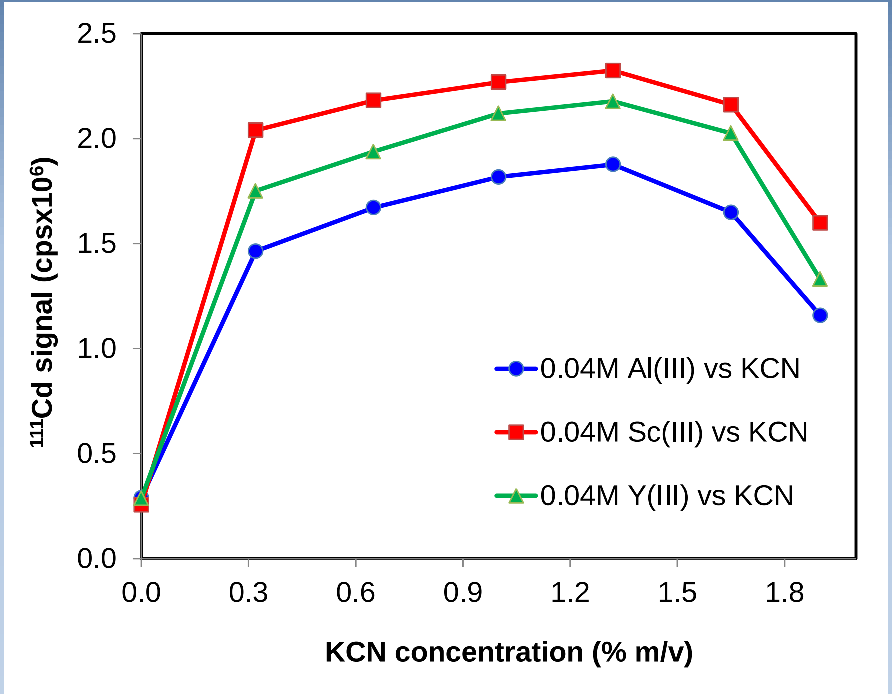
Preliminary information-subject to revision. Not for citation or distribution.

Effect of KCN concentration on CVG



The effect of KCN concentration on CVG for 10 µg L^{-1} Cd(II) in multielement solution when reacted with 0.04 mol L^{-1} solutions of Al(III), Sc(III), and Y(III). Sample acidity = 4% (v/v) HCl; $NaBH_4$ = 2% m/v, MC-1 = 5 cm; MC-2 = 15 cm.

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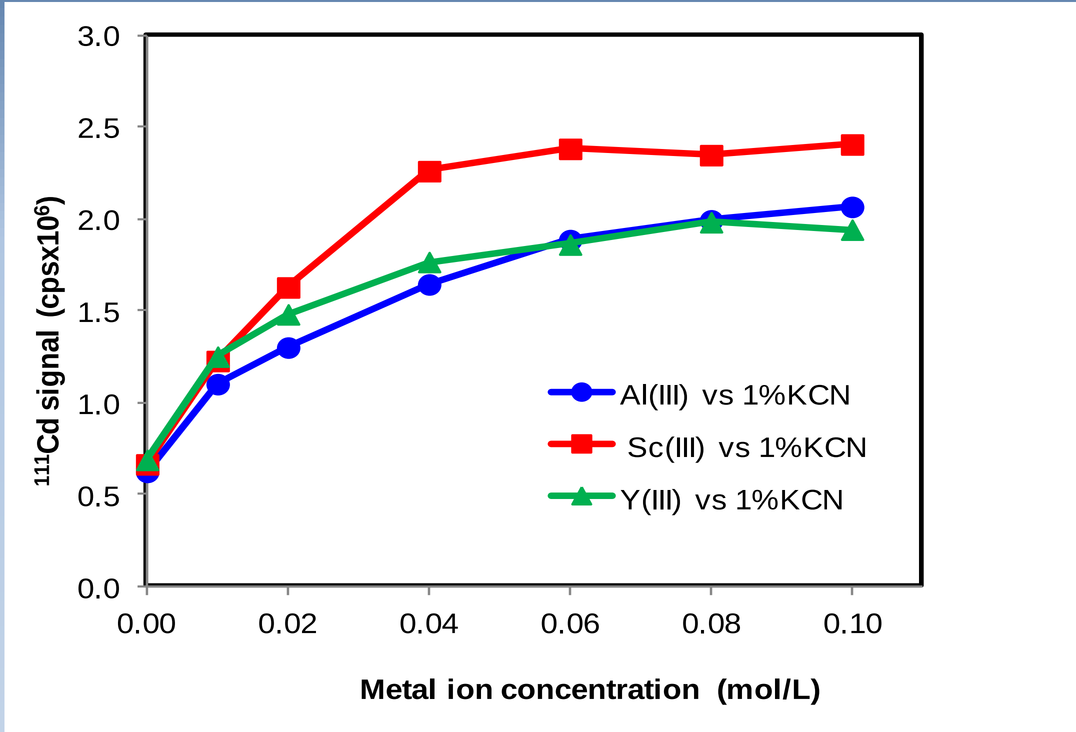
Optimization of Al(III), Sc(III), and Y(III) concentrations



Effects of Al(III), Sc(III), Y(III) concentrations on CVG for 10 µg L^{-1} Cd(II) in multielement solution. Sample acidity = 4% HCl; $NaBH_4$= 2% m/v, MC-1 = 5 cm; MC-2 = 15 cm.

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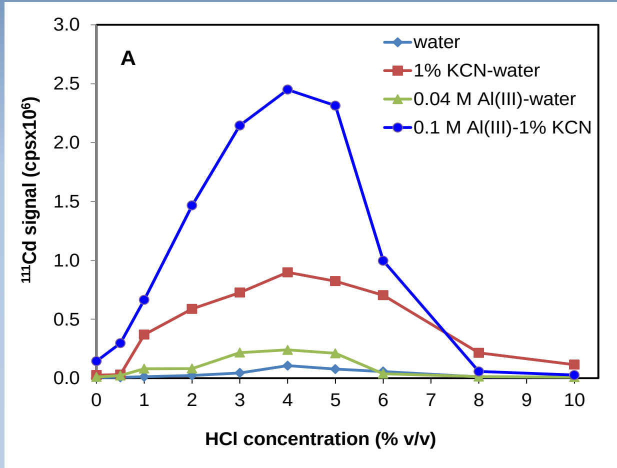
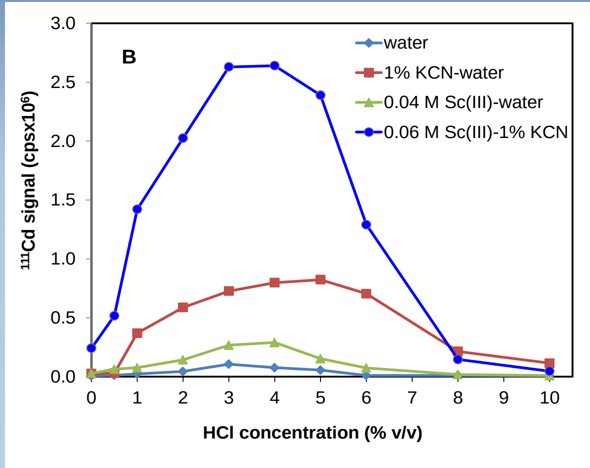
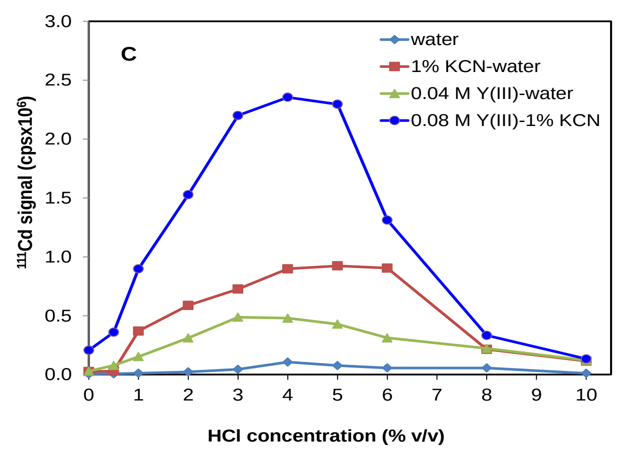
Preliminary information-subject to revision. Not for citation or distribution.

Verification of CVG performance with optimized conditions







HCl - Al(III) - KCN

HCl - Sc(III) - KCN

HCl - Y(III) - KCN

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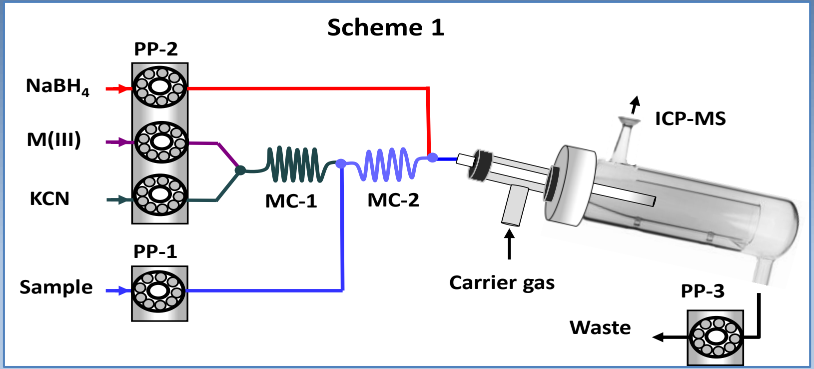
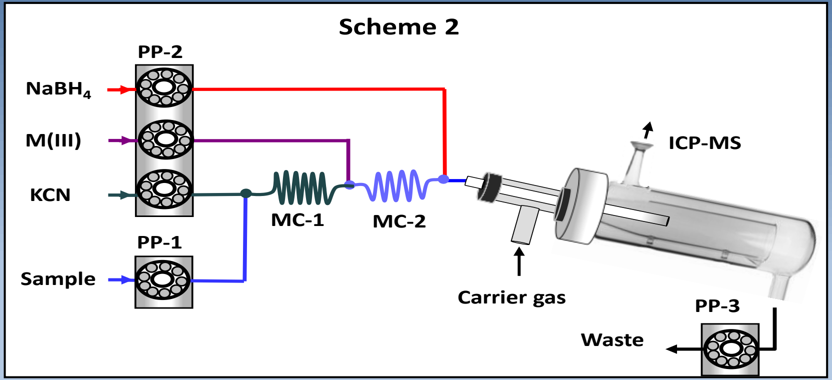
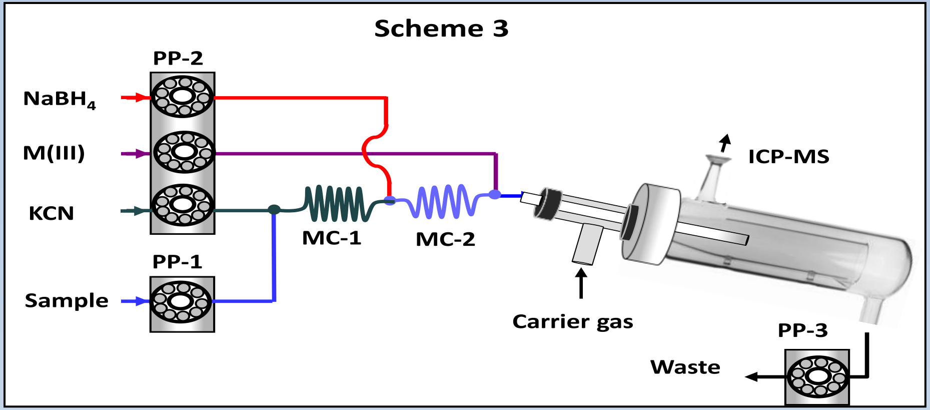
Role of Al(III), Sc(III), and Y(III) on CVG







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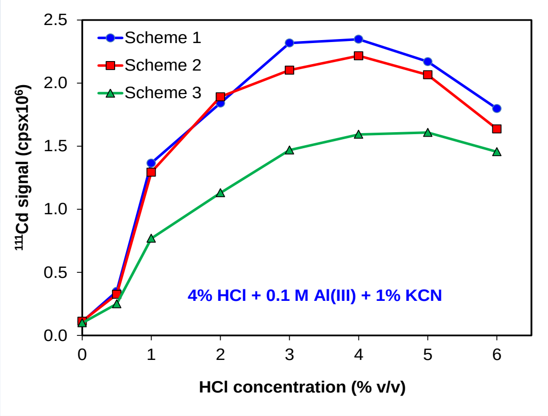
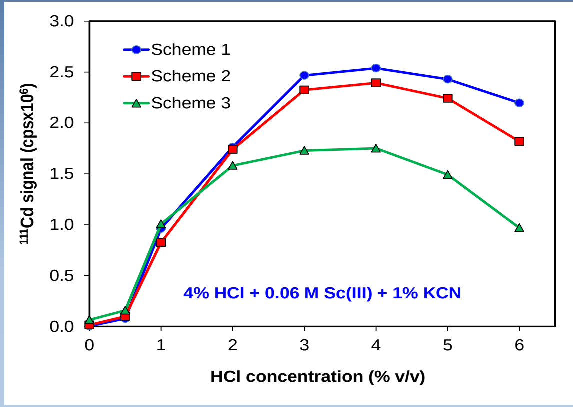
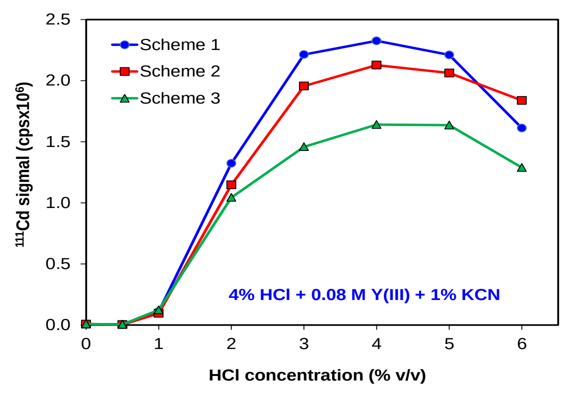
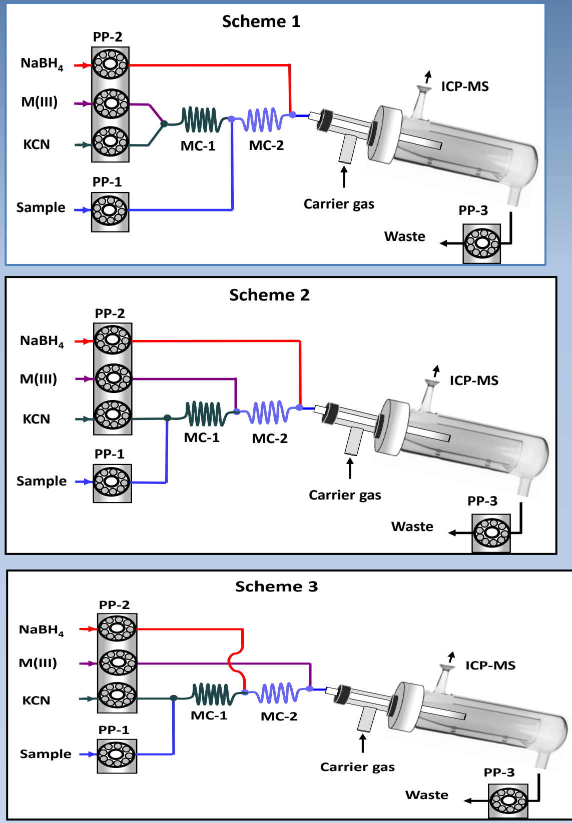
Preliminary information-subject to revision. Not for citation or distribution.

Roles of Al(III), Sc(III), and Y(III) on Cd CVG









Signal profiles for CVG of 10 µg L^{-1} Cd(II) using three different manifolds.

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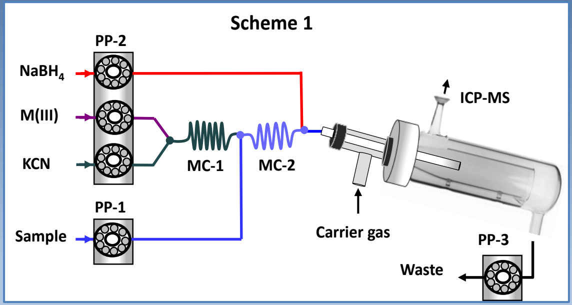
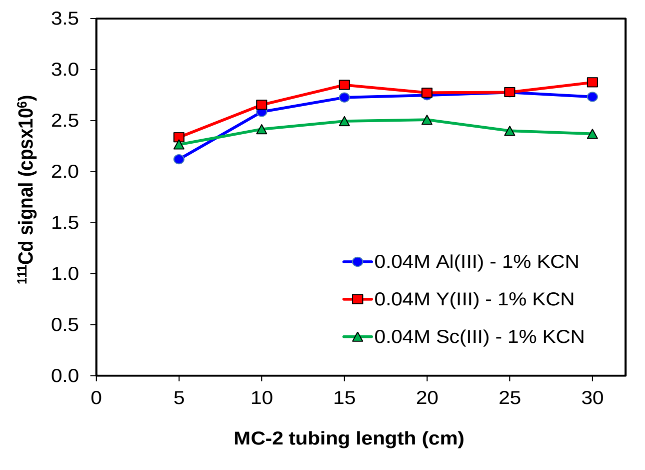
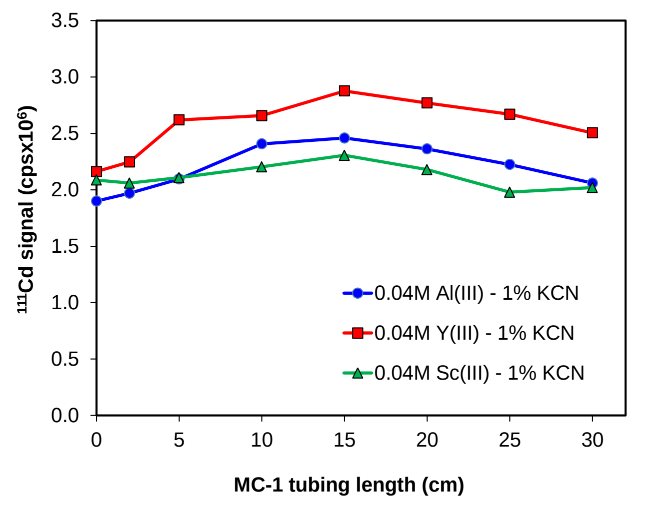
Effects of MC-1 and MC-2 mixing line lengths on CVG





- MC-2 line of 10 to 20 cm was optimum
- MC-2 tubing length was kept at 15 cm



- Signals tended to increase up to 15 cm MC-1 line
- A 5-cm long MC-1 was sufficient to achieve desired sensitivity

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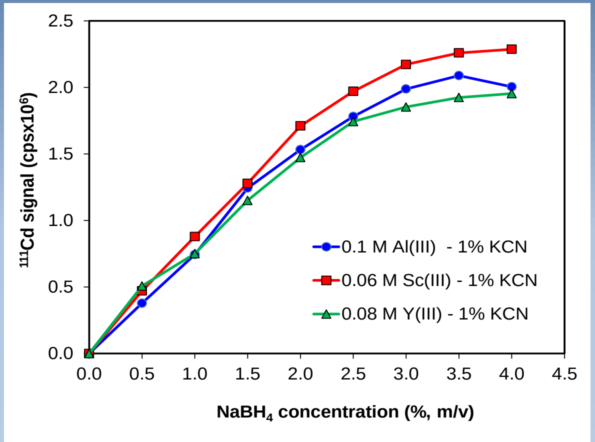
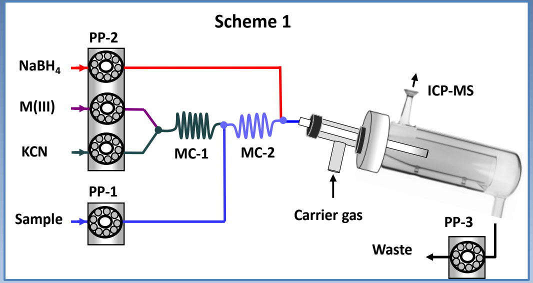
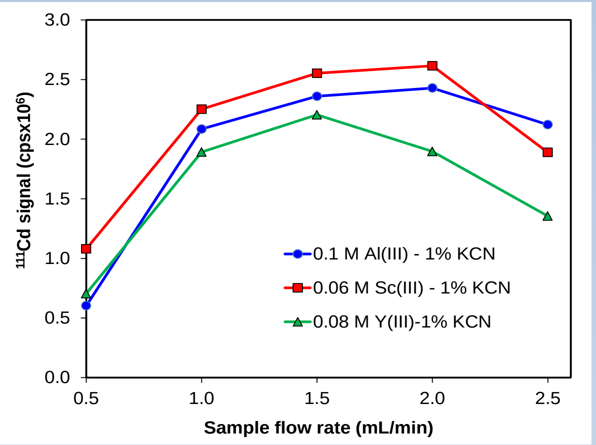
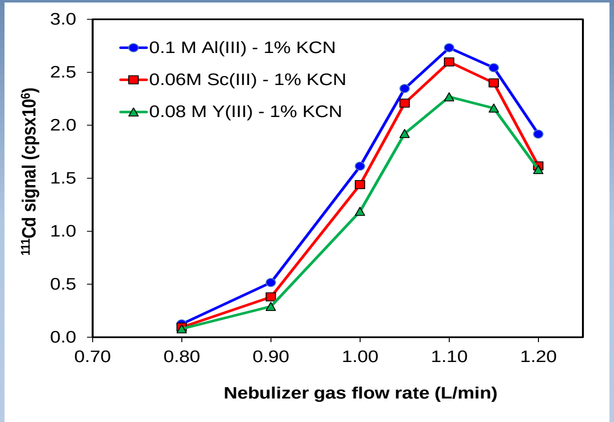
Optimization of $NaBH_4$, sample and nebulizer gas flow rates



3% $NaBH_4$ was sufficient to obtain maximum signals







Optimum nebulizer gas flow rate was found to be 1.10 to 1.15 L min^{-1}

Sample flow rate was kept constant at 1.0 mL min^{-1} to minimize sample consumption

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Effects of transition metals on Cd CVG

Element	Concentration (µg mL^{-1})	Relative signal (%)		
		Al(III)-KCN	Sc(III)-KCN	Y(III)-KCN
Co(II)	0.1	94 ± 3	78 ± 3	78 ± 2
	0.5	93 ± 5	74 ± 4	77 ± 3
	1.0	103 ± 4	65 ± 2	78 ± 3
Cr(III)	0.1	103 ± 2	98 ± 5	93 ± 3
	0.5	96 ± 2	99 ± 5	102 ± 4
	1.0	98 ± 6	98 ± 2	97 ± 6
Cu(II)	0.1	99 ± 2	102 ± 4	92 ± 5
	0.5	91 ± 3	93 ± 5	87 ± 3
	1.0	67 ± 3	90 ± 5	73 ± 2
Fe(III)	0.1	88 ± 4	96 ± 6	93 ± 2
	0.5	65 ± 3	78 ± 3	88 ± 5
	1.0	63 ± 2	88± 4	92 ± 6

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Preliminary information-subject to revision. Not for citation or distribution.

Effects of transition metals on Cd CVG – cont'd

Element	Concentration (μg mL^{-1})	Relative signals (%)		
		Al(III)-KCN	Sc(III)-KCN	Y(III)-KCN
Mn(II)	0.1	95 ± 3	95 ± 2	103 ± 4
	0.5	90± 3	93 ± 6	98 ± 3
	1.0	94 ± 2	115 ± 4	110 ± 6
Ni(II)	0.1	173± 6	101 ± 2	118 ± 6
	0.5	128 ± 7	76 ± 3	88 ± 4
	1.0	136 ± 5	66 ± 3	73 ± 3
Zn(II)	0.1	98 ± 5	92 ± 3	93 ± 2
	0.5	90 ± 2	95 ± 4	105 ± 6
	1.0	93 ± 4	99 ± 4	115 ± 5

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Effects of hydride forming elements on Cd CVG

Element	Concentration ($\mu g\ mL^{-1}$)	Relative signals (%)		
		Al(III)-KCN	Sc(III)-KCN	Y(III)-KCN
As(III)	0.1	94 ± 3	92 ± 2	95 ± 3
	0.5	91 ± 4	90 ± 3	103 ± 5
Bi(III)	0.1	99 ± 2	103 ± 4	99 ± 4
	0.5	74 ± 3	82 ± 5	72 ± 3
Pb(II)	0.1	62 ± 2	72 ± 4	73 ± 4
	0.5	36 ± 3	38 ± 4	30 ± 5
Sb(III)	0.1	100 ± 4	102 ± 3	98 ± 3
	0.5	93 ± 5	103 ± 5	103 ± 3
Se(IV)	0.1	82 ± 6	94 ± 2	78 ± 5
	0.5	62 ± 3	60 ± 5	50 ± 3
Sn(II)	0.1	98 ± 5	102 ± 5	102 ± 3
	0.5	93 ± 3	93 ± 4	102 ± 6

Al(III)/Ni + KCN for alleviating effects

Element	Concentration (μg mL^{-1})	Relative signals (%) Al(III)-KCN
Fe(III)	0.1	99 ± 3
	0.5	101± 2
	1.0	103 ± 4
Cu(II)	0.1	101 ± 3
	0.5	93 ± 4
	1.0	98 ± 3
Se(IV)	0.1	99 ± 3
	0.2	101 ± 4
	0.5	98 ± 4
Pb(II)	0.05	92 ± 4
	0.1	82 ± 3
	0.2	58 ± 5
	0.5	37 ± 2

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Effects of alkali and alkaline earth elements on Cd CVG

Element	Concentration (µg mL^{-1})	Al(III)-KCN	Sc(III)-KCN	Y(III)-KCN
Ca	1000	98 ± 6	101 ± 5	99 ± 6
K	1000	101 ± 3	98 ± 3	102 ± 4
Mg	1000	104 ± 5	99 ± 5	106 ± 6
Na	1000	106 ± 4	98 ± 6	103 ± 3

CVG efficiency was not affected from alkali and alkaline earth elements (Ca, Mg, K, and Na) at 1000 µg mL^{-1} levels. Relative response varied from 98% to 106%.

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Analytical figures of merits of CVG for Al(III), Sc(III) and Y(III)

Remarks	Al(III)-KCN	Sc(III)-KCN	Y(III)-KCN
Blanks (cps)	15000-25000	40000-50000	55000-70000
LOD (ng L^{-1})	5.2	6.3	7.8
Calibration curve	$y = 2989x + 0.007$ ($R^2 = 0.9999$)	$y = 2938x + 0.001$ ($R^2 = 0.9998$)	$y = 2368x + 0.0117$ ($R^2 = 0.9995$)
Enhancement	20	20	17

Calibration curve was constructed with standards from 0 to 2 ppb in 4% HCl. Enhancement is with respect to direct nebulization.

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Method validation with SRMs - CVG-ICP-MS (n = 4)

CVG setup	Isotope	CASS-4 Nearshore seawater (µg/L)	SLEW-3 Estuarine water (µg/L)	SRM 1400 Bone ash (µg/g)	SRM 2781 Domestic sludge (µg/g)
HCl - Al(III) - KCN	^{110}Cd	0.027 ± 0.005	0.044 ± 0.007	0.033 ± 0.006	12.2 ± 2.2
	^{111}Cd	0.026 ± 0.003	0.048 ± 0.005	0.035 ± 0.005	12.4 ± 1.3
HCl - Sc(III) - KCN	^{110}Cd	0.029 ± 0.005	0.043 ± 0.005	0.028± 0.006	12.6 ± 1.8
	^{111}Cd	0.028 ± 0.006	0.048 ± 0.008	0.029 ± 0.003	12.4 ± 0.9
HCl - Y(III) - KCN	^{110}Cd	0.023 ± 0.005	0.044 ± 0.006	0.026 ± 0.006	12.1 ± 2.1
	^{111}Cd	0.022 ± 0.006	0.047 ± 0.005	0.029 ± 0.005	12.2 ± 2.2
	Certified value	0.026 ± 0.003	0.048 ± 0.004	(0.03)	12.78 ± 0.72

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Summary / Conclusions

- A new CVG method was developed for the determination of Cd by ICP-MS
- Al(III), Sc(III), and Y(III) enhance Cd CVG in the presence of KCN as complexing agent
- Methods are robust and easy to use
- HCl-Al(III)-KCN is most affordable and has low background signals compared with Sc(III) and Y(III) settings

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