Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

On a single method for determining As and Hg in dietary supplements by CVG-MIP OES: optimization of the multimode sample introduction system

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Supplementary Material

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Table S1. Classification, sample code, dosage form, and active ingredients of dietary supplements used in this study.

Classification	Sample code	Dosage form	Active ingredients	Origin
Vitamins and minerals	VM-1	Tablet	Vitamins A, B1, B2, B3, B5, B6, B7, B9, B12, C, D3, and K, MgO, Cr, Cu, Mb, Mn, Se, and Zn	Brazil
Vitamins and minerals	VM-2	Tablet	Vitamins A, B1, B2, B3, B6, B9, B12, C, and D, $FeSO_4$, $ZnSO_4$, $MnSO_4$, and calcium D-pantothenate	Brazil
Vitamins and minerals	VM-3	Tablet	Vitamins A, B1, B2, B5, B6, B7, B9, B12, C, D3, E, and K, $CaCO_3$, $C_4H_2FeO_4$, KI, MgO, ZnO, Na_2Se, $CuSO_4$, $MgSO_4$, $CrCl_3$, and Na_2MoO_4	USA
Vitamins and minerals	VM-4	Capsule	Vitamins D3 and E, oyster shell $CaCO_3$, $C_4H_8N_2MgO_4$, $Zn(C_2H_4NO_2)_2$, $C_5H_{11}NO_2Se$, and SiO_2	Brazil
Minerals	MN-1	Tablet	$CaCO_3$, MgO, $ZnSO_4$, $C_8H_9NaO_7$, $C_{18}H_{36}O_2$, TiO_2, and $MgSiO_3$	USA
Minerals	MN-2	Capsule	Calcium amino acid chelate, KH_2PO_4, KI, magnesium amino acid chelate, zinc amino acid chelate, $C_5H_{11}NO_2Se$, copper amino acid chelate, manganese amino acid chelate, $Cr(C_6H_4NO_2)_3$, Mo, KCl, H_3BO_3, vanadium amino acid chelate, glutamic acid, rice protein, parsley leaf, alfalfa leaf, horsetail, watercress, dandelion root, yellow dock root, and chamomile	USA
Amino acids	AA-1	Powder	Creatine monohydrate	Brazil
Amino acids	AA-2	Powder	Taurine, vitamins B6, B12, and PP, Beta-5 (*beta vulgaris L.*, powdered beet, and vitamin B5), NO2Drive (watermelon pulp, vitamin B2, vitamin B3, and calcium L-ascorbate), glucuronolactone, and caffeine	Brazil
Amino acids	AA-3	Capsule	L-leucine, L-isoleucine, and L-valine	Brazil
Amino acids	AA-4	Capsule	L-theanine	USA
Botanicals	BT-1	Capsule	Ginseng extract (*panax ginseng*), rice bran, and oat fiber	USA
Botanicals	BT-2	Capsule	Guarana (*paullinia cupana*) and açaí (*euterpe oleracea*) flavoring, catuaba (*anemopaegma mirandum*), cocoa (*theobroma cacao*), and ginseng (*panax ginseng*) extracts, vitamins A, B1, B2, B3, B5, B6, B9, B12, C, E and K2, Cu, Fe, Cr, Mn, Mo, Se, and Zn	Brazil
Botanicals	BT-3	Capsule	Ginseng extract (*panax ginseng*) and tribulus fruit powder (*tribulus terrestris L.*)	Brazil

Table S2. Procedures and experimental conditions evaluated for the pre-reduction of As(V) to As(III).

Procedure (matrix)	**Conditions**	**Ref**
A (Iron and steel)	0.6% w v^{-1} of L-cysteine (0.05 mol L^{-1}) in 1 mol L^{-1} of HCl for 5 min	1
B (Botanicals)	10 g L^{-1} of L-cysteine (0.08 mol L^{-1})	2
C (Liver, soil and water)	1% w v^{-1} of thiourea (0.13 mol L^{-1}) for 30 min	3
D (Foods)	2% w v^{-1} of thiourea (0.26 mol L^{-1}) in 10% v v^{-1} HCl (1.2 mol L^{-1}) for 15 min	4
E (Standard solution)	0.15% v v^{-1} (0.02 mol L^{-1}) of thiourea in 5 mol L^{-1} of HCl for 1 h.	5

Table S3. Conditions and LODs reported in the literature and in this work.

Sample matrix	Analytes	Sample introduction system	Conditions	Pre-reduction of As(V) method	LOD	Ref.
Dietary supplement	As and Hg	MSIS	- N_2-MIP-OES - 0.6% w/v $NaBH_4$, 1 mol L^{-1} HCl and flow-rate solutions of 2.2 mL min^{-1}	- 2% w/v thiourea in 10% v/v HCl - Reaction time of 15 min	**As[a]:** 0.3 μg L^{-1} **Hg[a]**: 0.9 μg L^{-1}	This work
Standard solution	As and Hg	Continuous hydride/cold vapor generation	- Low power Ar-He-MIP-OES - 1% w/v $NaBH_4$, 2 mol L^{-1} HCl and flow-rate solutions of 1 mL min^{-1}	No	**As[b]**: 4.1 μg L^{-1} **Hg[b]:** 1.4 μg L^{-1}	6
Geological, biological and water reference materials	As and Hg	Continuous hydride/cold vapor generation	- Low power (μ-USN-DCS)-Ar-He-MIP-OES - 1% w/v $NaBH_4$, 1.5 mol L^{-1} HNO_3 and flow-rate solutions of 15 μL min^{-1}	- 1 mol L^{-1} thiourea - Reaction time of 40 min	**As[b]:** 1.2 μg L^{-1} **Hg[b]:** 3.0 μg L^{-1}	7
Analgesic activity agent	As and Hg	MSIS	- N_2-MIP-OES - **As:** 0.4% w/v $NaBH_4$ and 1 mol L^{-1} HCl; **Hg:** 1.5% w/v $NaBH_4$ and 5% v/v HCl; Flow-rate solutions was not evaluated	No	**As[b]:** 11 μg L^{-1} **Hg[b]:** 1.3 μg L^{-1}	8
Fish tissue	As and Hg	MSIS	- N_2-MIP-OES - 1% w/v $NaBH_4$. HCl concentration was not informed. Flow-rate solution was not evaluated.	No	**As[b]:** 2 μg L^{-1} **Hg[b]**: 0.2 μg L^{-1}	9

Chinese green tea	As	Continuous hydride generation	- Low power Ar-MIP-OES - 0.5% w/v $NaBH_4$, 3 mol L^{-1} HCl and flow-rate solutions of 1.1 mL min^{-1}	No	1.3 µg L^{-1}[b]	10
Standard solution	As	Continuous hydride generation	- Low power Ar-MIP-OES - 5% w/v $NaBH_4$, 1.2 mol L^{-1} HCl and flow-rate solutions of 0.1 mL min^{-1}	No	50 µg L^{-1}[b]	11
Agricultural samples	As	MSIS	- N_2-MIP-OES - 0.6% w/v $NaBH_4$ and 1 mol L^{-1} HCl	- 1% w/v KI in 1 mol L^{-1} HCl - Reaction time of 1 h	0.46 µg L^{-1}[d]	12
Inorganic fertilizers	Hg	MSIS	- N_2-MIP-OES - 10% w/v $SnCl_2$, 10 mol L^{-1} HCl, and flow-rate solutions of 9.0 mL min^{-1} (sample) and 2.5 mL min^{-1} (acid and reductant solutions)	-	0.3 µg L^{-1}[c]	13
Leather and fur	Hg	MSIS	- N_2-MIP-OES - 2% w/v $NaBH_4$, HCl was not used, and flow-rate solutions of 1 mL min^{-1}	-	2.0 µg L^{-1}[b]	14

LODs obtained by [a] $LOD = 3\sigma_{blank} + \bar{x}_{blank}$, [b] $LOD = 3\sigma_{blank}$ or [c] $LOD = 3\sigma_{blank}/S$. [d]Calculation not specified.

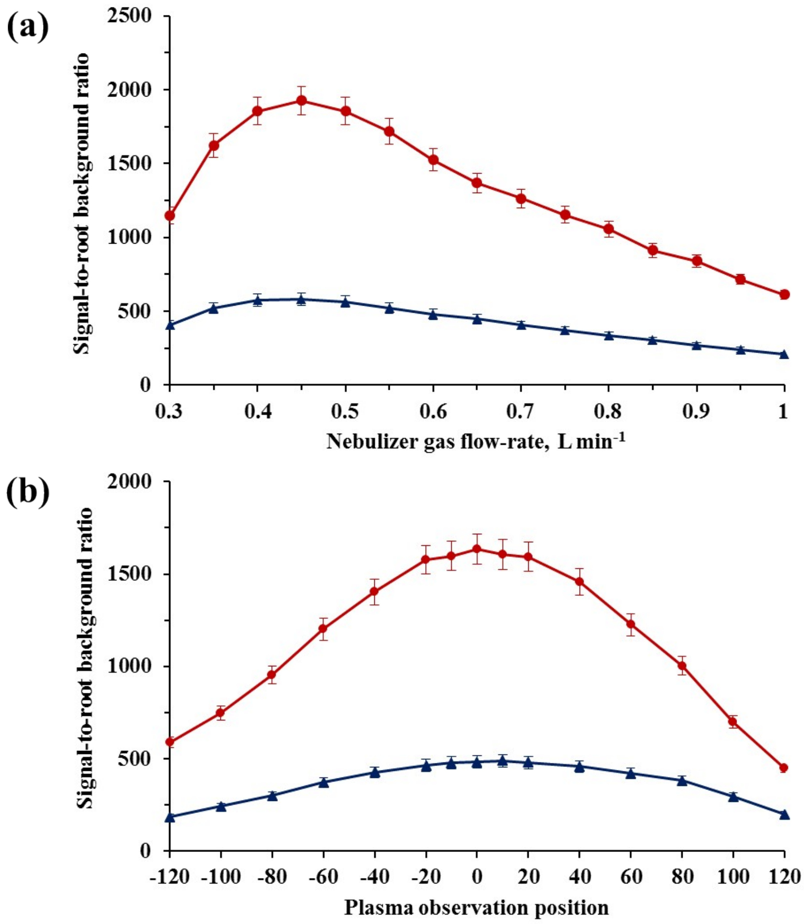

Fig S1. Influence of the a) nebulizer gas flow-rate and b) plasma observation position in the emission signal intensities (signal-to-root background ratio) of As(III) (blue) and Hg(II) (red) by CVG-MIP-OES (n = 3).

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