ELECTRONIC SUPPLEMENTARY INFORMATION

Unified analysis method for total and inorganic As determination in foodstuffs by hydride generation high-resolution continuum source quartz tube atomic absorption spectrometry

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This online resource contains the following data:

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2. Sample preparation procedure for the determination of tAs and iAs by HG-HR-CS-QTAAS
3. Influence of experimental conditions on arsine generation from As(III) and absorption signal
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1. Operation of the HG-HR-CS-QTAAS analytical system

The batch mode hydride generation system HS55 consisted of a PTFE reaction cell ensuring gas-liquid separation, a variable speed peristaltic pump with single channel to supply the derivatization reagent ($NaBH_4$ solution) and an electric oven equipped with a conventional quartz tube atomizer (140 mm length, 15 mm i.d.) with removable quartz windows at the ends, heated at 950 ± 10 °C for arsine atomization. A three-way valve served to control the Ar stream through the system. The reaction cell and the quartz tube were connected by a 120 cm length Nafion dryer tube to remove the moister from the wet carrier Ar–arsine stream. The high-resolution spectrometer ContrAA 300 is equipped with a high-intensity xenon short-arc lamp with continuum emission (185–900 nm), a high-resolution double monochromator (2 pm FWHM) and a charge-coupled device (CCD) detector with 512 pixels. A number of 200 pixels were used to view the As 193.696 nm line and spectral environment of ± 0.1 nm. The signal of the As 193.696 nm line was integrated over 5 pixels (CP ± 2). The operation procedure,

although discontinuous, was simple and involved pipetting of 5 mL sample aliquots into the reaction cell, air purging from the cell reaction-quartz tube assembly with an Ar stream, then pumping a volume of 3.5 mL $NaBH_4$ solution. The arsine generated in the reaction cell together with H_2 and O_2 traces was purged from the liquid with 6 L h^{-1} Ar and directed through the Nafion tube to the QTA. The free As atoms generated in the quartz tube absorbed the specific wavelength of 193.696 nm emitted by the Xe continuum radiation source passing through the QTA. The transmitted radiation falls on the CCD detector and the absorption spectrum was recorded over the range ± 0.1 nm in the vicinity of the analytical line As 193.696 nm. Background correction was achieved by subtracting the signal of the appropriate blank solution (e.g. 0.2% L – cysteine in HCl (pH = 2.00 ± 0.01)) from the integrated absorption of As over the 5 pixel bandwidth in the centre of the spectral window. Spectra were recorded with an integration time of 40 s and the As signal was measured as both peak height and area.

2. Sample preparation procedure for the determination of tAs and iAs by HG-HR-CS-QTAAS

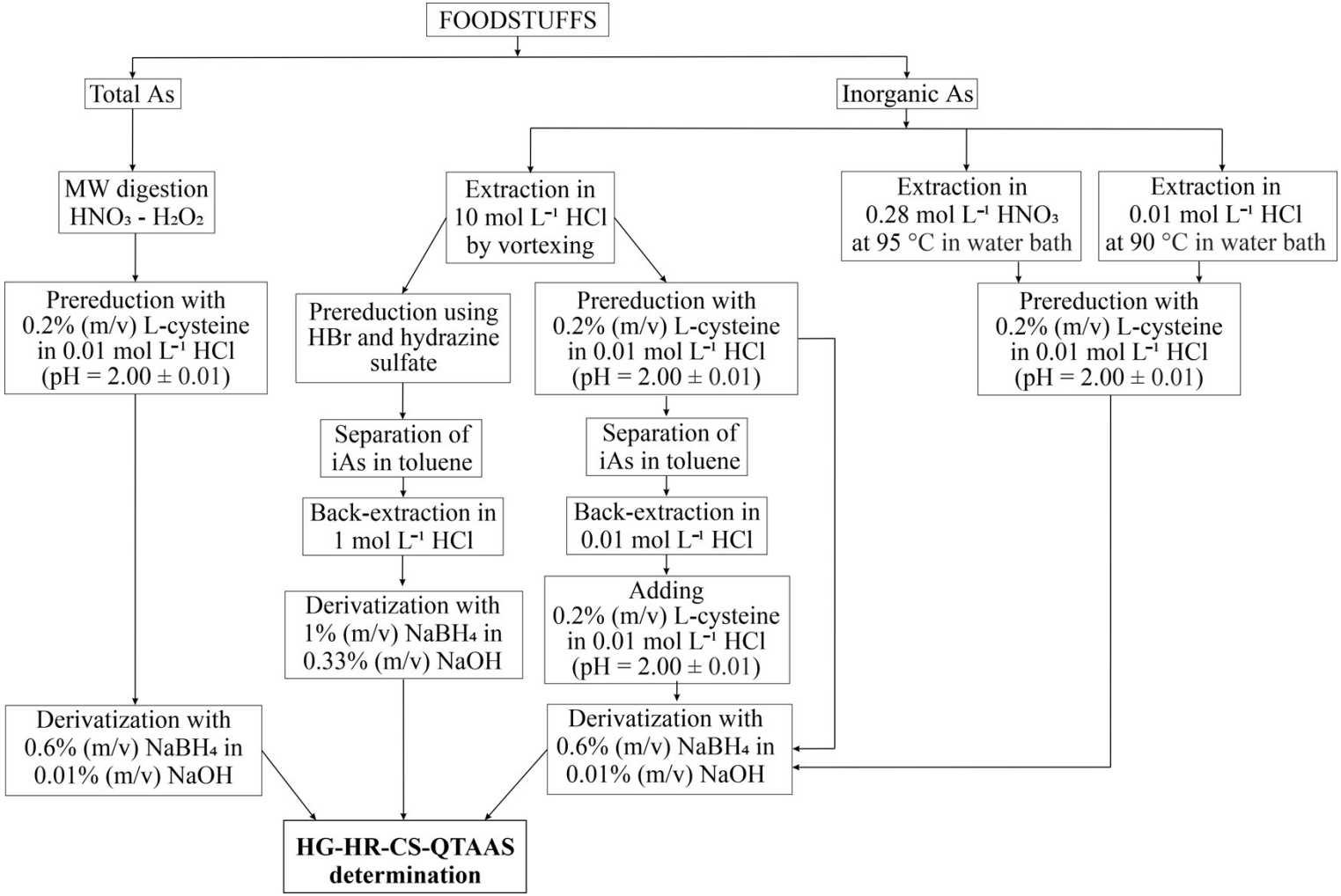

Fig. S1. Schematic representation of sample preparation procedures for foodstuffs for the determination of tAs and iAs by the HG-HR-CS-QTAAS method

3. Influence of the experimental conditions for arsine generation from As(III) on the absorption signal

The effects of the concentrations of NaOH, sample pH, $NaBH_4$, L-cysteine, antifoam agent and volume of $NaBH_4$ solution on the As absorption signal for 5 mL aliquots containing 2 µg L^{-1} As(III) are presented in Figs. S2–S7.

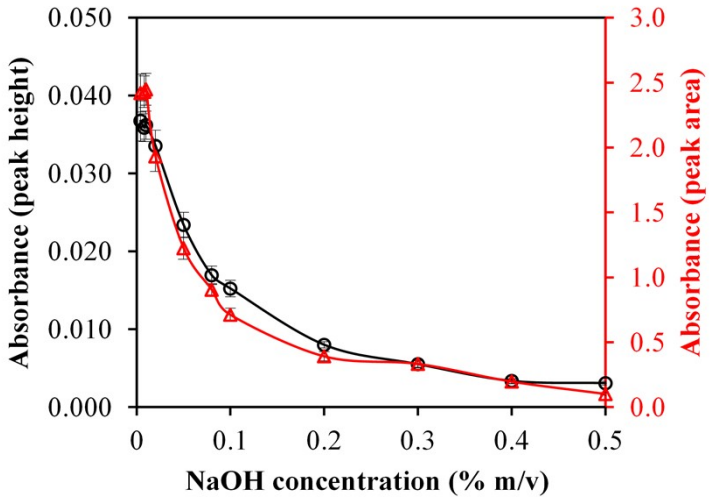

Fig. S2. Effect of NaOH concentration on the As absorption signal. Sample: 5 mL solution containing 2 µg L^{-1}As(III) in 0.2% (m/v) L–cysteine and HCl (pH = 2.00 ± 0.01); 3.5 mL 0.6% (m/v) $NaBH_4$ solution. Error bars correspond to SD for five successive measurements.

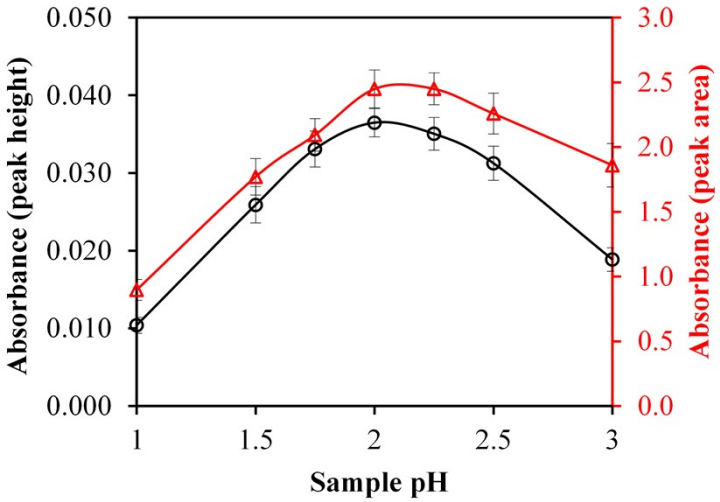

Fig. S3. Effect of sample pH on the As absorption signal. Sample: 5 mL solution containing 2 µg L^{-1}As(III) in HCl (pH = 2.00 ± 0.01); 3.5 mL 0.6% $NaBH_4$ solution stabilized in 0.01% NaOH. Error bars correspond to SD for five successive measurements.

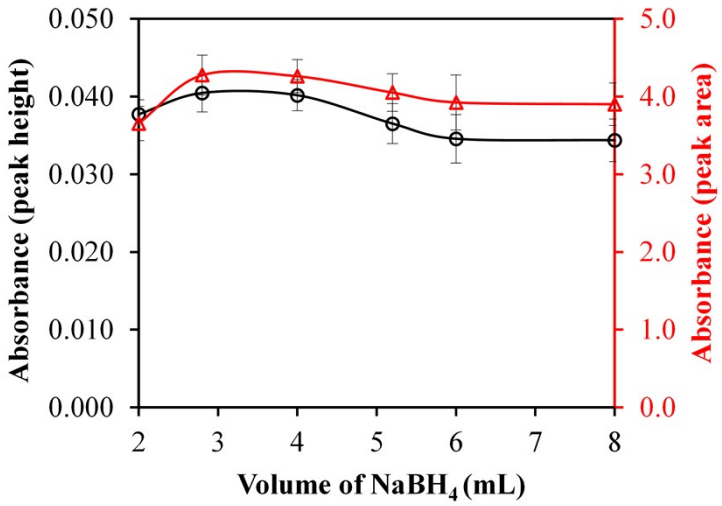

Fig. S4. Effect of the volume of 0.6% $NaBH_4$ solution stabilized in 0.01% NaOH on the As absorption signal. Sample: 5 mL solution containing 2 μg L^{-1}As(III) in HCl (pH = 2.00 ± 0.01). Error bars correspond to SD for five successive measurements.

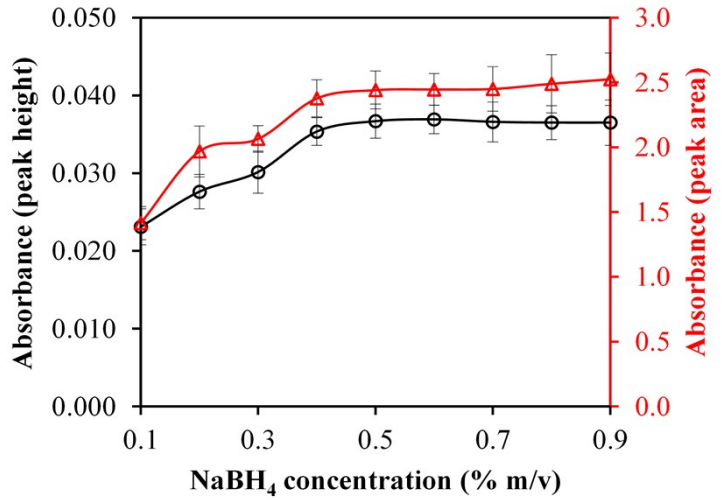

Fig. S5. Effect of $NaBH_4$ concentration stabilized in 0.01% (m/v) NaOH on the As absorption signal. Sample: 5 mL solution containing 2 μg L^{-1} As(III) in 0.2% (m/v) L–cysteine and HCl (pH = 2.00 ± 0.01); 3.5 mL 0.6% $NaBH_4$ solution stabilized in 0.01% NaOH. Error bars correspond to SD for five successive measurements.

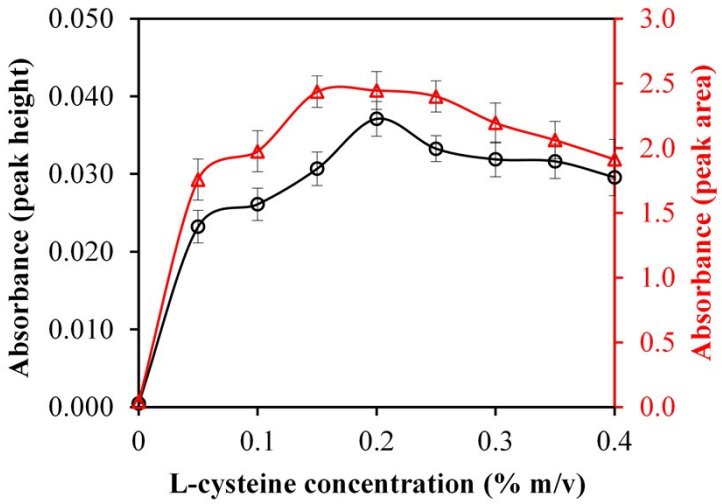

Fig. S6. Effect of L–cysteine concentration on the As absorption signal. Sample: 5 mL solution containing 2 µg L^{-1}As(III) in HCl (pH = 2.00 ± 0.01); 3.5 mL 0.6% $NaBH_4$ solution stabilized in 0.01% NaOH. Error bars correspond to SD for five successive measurements.

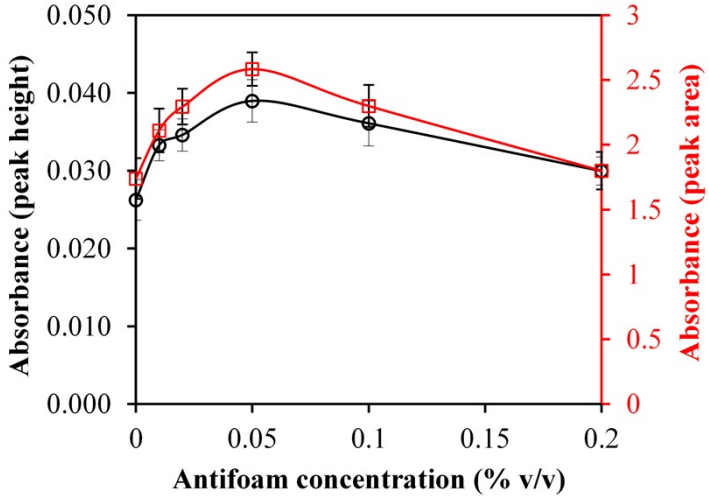

Fig. S7. Effect of antifoam agent concentration in 0.6% (m/v) $NaBH_4$ stabilized in 0.01% (m/v) NaOH on the As absorption signal. Sample: 5 mL solution containing 2 µg L^{-1} As(III) in 0.2% L-cysteine and HCl (pH = 2.00 ± 0.01); 3.5 mL 0.6% $NaBH_4$ solution stabilized in 0.01% NaOH. Error bars correspond to SD for five successive measurements.

The increase of NaOH concentration above 0.01% (m/v) in the $NaBH_4$ solution (Fig. S2) induced an exponential decrease of As absorption. The optimal pH in sample solution was 2.00 ± 0.01 (Fig. S3). The absorption signal decreased when pH was > 2, as a result of the decrease in the concentration of hydronium ions involved in the kinetics of arsine generation, and lower amount of hydrogen generating free radicals necessary for arsine atomization in QT. Similarly, a decrease of the As absorption was observed when using volumes of $NaBH_4$ solution higher than 3.5 mL for 5 mL sample (pH = 2.00 ± 0.01), as a result of HCl neutralization by NaOH, and thereby a decreased rate of

arsine generation (Fig. S4). The concentration of $NaBH_4$ should be in the range 0.5–0.9% (m/v), so we decided for 0.6% (Fig. S5). L-cysteine used as prereductant was also involved in arsine generation from As(III), since the absorption response increased with concentration up to 0.15% (m/v). The level of 0.2% (m/v) L-cysteine in the sample solution was selected as optimal in the study (Fig. S6). The optimal concentration of antifoam agent in the $NaBH_4$ solution was established as 0.05% (v/v), above which a linear decrease of the absorption signal was observed (Fig. S7). The antifoam agent was necessary in all sample preparation procedures for iAs determination, when the separation by liquid-liquid extraction in the toluene-HCl system was not applied, to prevent foaming caused by the reaction between proteins and $NaBH_4$.

4. Inter-day reproducibility for the calibration curve and LOD in peak height absorbance measurement

Table S1. Inter-day reproducibility of the calibration curve and LOD for 25 days for As determination in 5 mL aliquot by HG-HR-CS-QTAAS in peak height measurement after prereduction with 0.2% L-cysteine in HCl (pH = 2.00 ± 0.01) and derivatization with 3.5 mL 0.6% (m/v) $NaBH_4$ in 0.01% (m/v) NaOH and 0.05% (v/v) antifoam agent

Characteristics of the calibration plot			Standard deviation of signal for blank solution (a.u.)	LOD ($\mu g\ L^{-1}$)
Intercept (a.u.)	Slope ($L\ \mu g^{-1}$)	R^2		
0.0011	0.0228	0.9996	0.0004	0.053
0.0007	0.0164	0.9978	0.0004	0.073
0.0002	0.0184	0.9995	0.0004	0.065
0.0044	0.0186	0.9979	0.0004	0.065
0.0010	0.0185	0.9995	0.0003	0.049
0.0016	0.0173	0.9988	0.0004	0.069
0.0012	0.0188	0.9992	0.0005	0.080
0.0004	0.0187	0.9981	0.0005	0.080
0.0012	0.0193	0.9997	0.0005	0.078
0.0003	0.0162	0.9952	0.0005	0.093
0.0021	0.0174	0.9976	0.0005	0.086
0.0011	0.0185	0.9989	0.0004	0.065
0.0026	0.0190	0.9994	0.0005	0.079
0.0007	0.0162	0.9996	0.0004	0.074
0.0071	0.0186	0.9967	0.0004	0.065
0.0012	0.0170	0.9987	0.0004	0.071
0.0026	0.0201	0.9995	0.0003	0.045
0.0012	0.0181	0.9981	0.0003	0.050
0.0011	0.0171	0.9997	0.0004	0.070
0.0002	0.0203	0.9991	0.0005	0.070
0.0004	0.0189	0.9996	0.0005	0.079
0.0038	0.0174	0.9996	0.0004	0.069
0.0008	0.0180	0.9988	0.0004	0.067
0.0055	0.0187	0.9984	0.0005	0.080
0.0013	0.0180	0.9958	0.0003	0.050
0.0018 ± 0.0007[a]	0.0183 ± 0.0006[a]	0.9986 ± 0.0005[a]	0.0004 ± 0.0001[a]	0.070 ± 0.005[a]

[a] Mean ± CI (confidence interval for 95% confidence level, n = 25 days)

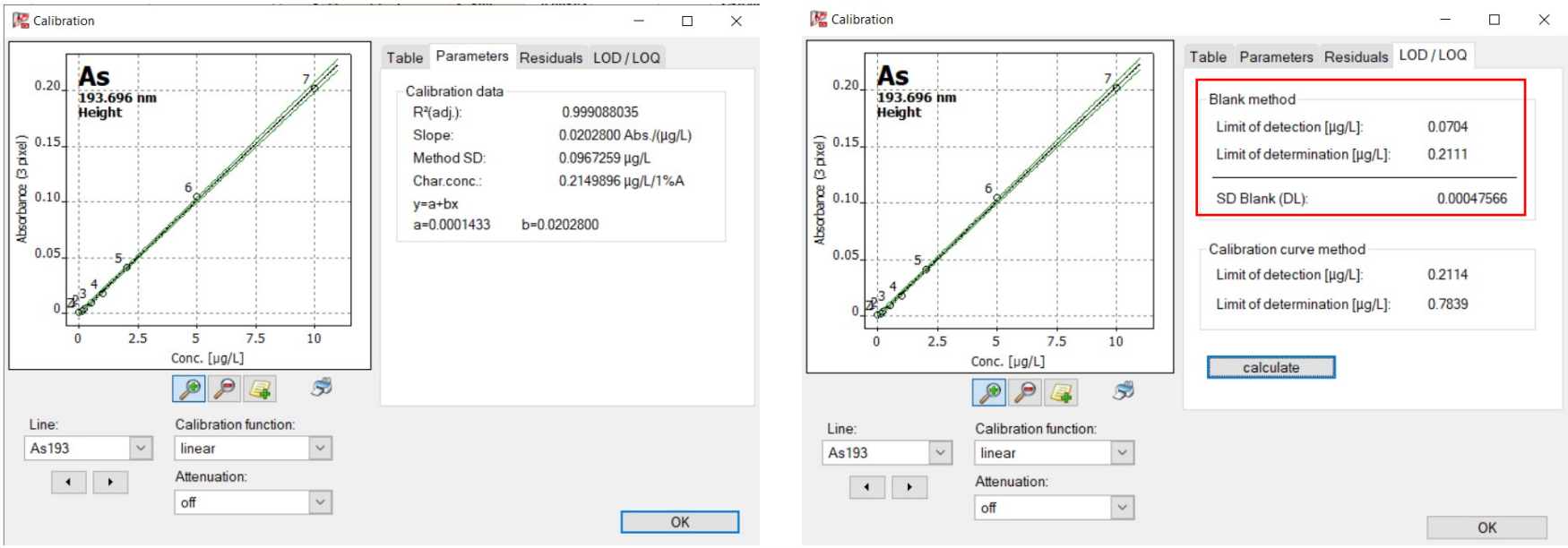

Fig. S8. Calibration curve and corresponding LOD (3σ criterion) for As 193.696 nm and peak height measurement

Table S2. Absorbance signals (n = 11) of the blank solution of 0.2% (m/v) L-cysteine in 0.01 mol L^{-1} HCl (pH = 2.00 ± 0.01)

Signal blank (a.u.)											Standard deviation (s_b) (a.u.)
0.00010	0.00068	0.00187	0.00118	0.00070	0.00052	0.00043	0.00067	0.00094	0.00038	0.00101	0.000476

5. Comparison of LODs of As obtained by HG-HR-CS-QFAAS and other methods

Table S3. Limit of detection of As obtained by HG-HR-CS-QTAAS using derivatization to arsine in 0.01 mol L^{-1} HCl (pH = 2.00 ± 0.01) in the presence of 0.2% (m/v) L-cysteine in comparison with other methods

Method[a]	As species	Samples	Preparation procedure	LOD	Reference[b]
HG-HR-CS-QTAAS	tAs	Food samples	Microwave-assisted digestion in HNO_3 – H_2O_2 and batch mode derivatization to arsine without preconcentration	0.0044 ± 0.0005 mg kg^{-1}	This paper
HG-HR-CS-QTAAS	iAs	Food samples	Extraction in different reagents (10 mol L^{-1} HCl; 0.01 mol L^{-1} HCl and 0.28 mol L^{-1} HNO_3) with and without separation of iAs species using double liquid-liquid extraction in the toluene-HCl system	0.0022 ± 0.0003 mg kg^{-1}	This paper
HG-HR-CS-QTAAS	tAs/iAs	Natural water	Batch mode derivatization without preconcentration	0.070 ± 0.006 µg L^{-1}	This paper
GFAAS	tAs	Mushrooms	Oxalic acid deep eutectic solvent extraction	0.50 µg L^{-1}	18
GFAAS	iAs	Water	Ultrasound-assisted supramolecular solvent microextraction and direct liquid sampling	0.2 µg L^{-1}	20
HR-CS-GFAAS	iAs	Fish and seafood	Direct solid sampling	0.05 µg kg^{-1}	21
ICP-MS/MS	tAs	Food	Microwave-assisted digestion in HNO_3 – H_2O_2 and derivatization without preconcentration	0.5 µg L^{-1}	15
ICP-MS	As(III), As(V)	Water	Solid phase microextraction	2.7; 3.2 ng L^{-1}	31

HG-AAS	As(III), As(V)	Natural water and Human biological samples	Ultrasound solid phase microextraction and derivatization	0.0248 µg L^{-1}	27
HG-AAS	iAs	Rice	Deep eutectic solvent ultrasound-assisted extraction and derivatization	1.7 µg L^{-1}	28
HG-AAS	tAs	Human urine	Alkaline digestion using $Na_2S_2O_8$ - NaOH solution	0.09 µg L^{-1}	49
HG-HR-CS-GFAAS	tAs	Surface water (lake and sea)	Solid phase microextraction and chemical vapor generation	0.25 µg L^{-1}	50
HG-CT-AAS	iAs, MMA, DMA	Baby food	Extraction in 3 mol L^{-1} HCl, derivatization and cryotrapping	0.44; 0.24; 0.16 µg kg^{-1}	26
HG-AFS	iAs	Rice and vegetables	Electrochemical HG approach	0.3 µg L^{-1}	29
HG-AFS	tAs, iAs	Rice	tAs extraction in 1:9 alkaline persulfate oxidation (3% m/v $K_2S_2O_8$ and 4% m/v NaOH) iAs extraction in 3 mL conc. HNO_3 + 1 mL H_2O_2 (2 h, 100ºC) Prereduction with 1% KI and 0.2% ascorbic acid and hydride generation in 4.8 mol L^{-1} HCl	3 ng g^{-1}; 1 ng g^{-1}	30
HG-ICP-OES	tAs/iAs	Rice	Ultrasound-assisted extraction in *aqua regia* without preconcentration	5.6 ng g^{-1}	31

[a] GFAAS – graphite furnace atomic absorption spectrometry; HR-CS-GFAAS – high-resolution continuum source graphite furnace atomic absorption spectrometry; HG-AAS – hydride generation atomic absorption spectrometry; HG-HR-CS-GFAAS – hydride generation high-resolution continuum source graphite furnace atomic absorption spectrometry; HG-AFS – hydride generation atomic fluorescence spectrometry; HG-CT-AAS – hydride generation cryotrapping atomic absorption spectrometry; ICP-MS – inductively coupled plasma mass spectrometry

[b] References in this table are those indicated in the paper

6. Mineral matrix composition of samples analyzed for tAs and iAs determination by HG-HR-CS-QTAAS

Table S4. Composition of the mineral matrix (mg L^{-1}) in the samples analyzed for tAs determination by the HG-HR-CS-QTAAS method

	Meat (fish muscle, pork and chicken) and organs															
	Na	K	Mg	Ca	Al	Fe	Cr	Mn	Co	Ni	Cu	Zn	Sr	Ba	Cd	Pb
Min	0.001	0.2	0.01	0.002	<0.003	0.03	<0.01	0.004	<0.02	<0.02	0.01	0.02	<0.007	<0.0004	0.001	<0.01
Max	10.0	36.9	3.4	21.1	<0.003	0.5	0.03	0.02	<0.02	<0.02	0.4	1.1	<0.007	<0.0004	0.003	<0.01
Mean	4.5	11.8	1.1	5.1	<0.003	0.2	0.01	0.01	<0.02	<0.02	0.2	0.2	<0.007	<0.0004	0.002	<0.01
SD	3.6	10.5	1.2	7.2	<0.003	0.2	0.004	0.01	<0.02	<0.02	0.2	0.3	<0.007	<0.0004	0.001	<0.01
	Rice, rice-based preparations for babies															
Min	0.03	0.3	0.001	0.01	<0.003	<0.006	<0.01	0.001	<0.02	<0.02	0.3	0.01	<0.007	<0.0004	<0.001	<0.01
Max	0.6	2.2	1.6	0.03	<0.003	<0.006	<0.01	0.05	<0.02	<0.02	0.7	0.2	<0.007	<0.0004	<0.001	<0.01
Mean	0.2	0.8	0.5	0.02	<0.003	<0.006	<0.01	0.02	<0.02	<0.02	0.5	0.1	<0.007	<0.0004	<0.001	<0.01
SD	0.1	0.6	0.4	0.01	<0.003	<0.006	<0.01	0.02	<0.02	<0.02	0.2	0.1	<0.007	<0.0004	<0.001	<0.01

Table S5. Composition of the mineral matrix (mg L^{-1}) in foodstuffs (meat, rice and rice-based products) analyzed for iAs determination by the HG-HR-CS-QTAAS method using extraction in 10 mol L^{-1} HCl

	Na	K	Mg	Ca	Al	Fe	Cr	Mn	Co	Ni	Cu	Zn	Sr	Ba	Cd	Pb
	Without separation															
Min	50	0.5	0.3	0.04	0.02	0.05	<0.01	<0.002	<0.02	<0.02	0.07	0.03	<0.007	0.002	<0.001	<0.01
Max	820	5.5	15	9.0	0.40	4.8	<0.01	<0.002	<0.02	<0.02	0.80	1.2	0.03	0.09	<0.001	<0.01
Mean	350	2.0	2.2	2.4	0.30	1.3	<0.01	<0.002	<0.02	<0.02	0.30	0.40	0.02	0.01	<0.001	<0.01
SD	230	1.6	3.2	1.7	0.12	1.0	<0.01	<0.002	<0.02	<0.02	0.20	0.30	0.21	0.04	<0.001	<0.01
	With separation in toluene															
Min	0.10	0.01	0.02	0.04	0.01	0.05	<0.01	<0.002	<0.02	<0.02	0.07	0.03	<0.007	<0.0004	<0.001	<0.01
Max	20.0	3.7	0.60	0.80	0.17	2.2	<0.01	<0.002	<0.02	<0.02	0.24	0.18	<0.007	<0.0004	<0.001	<0.01
Mean	2.4	0.70	0.30	0.40	0.07	1.2	<0.01	<0.002	<0.02	<0.02	0.15	0.11	<0.007	<0.0004	<0.001	<0.01
SD	5.8	1.0	0.20	0.30	0.05	0.50	<0.01	<0.002	<0.02	<0.02	0.06	0.04	<0.007	<0.0004	<0.001	<0.01

Table S6. Composition of the mineral matrix (mg L^{-1}) in foodstuffs (meat, rice and rice-based products) analyzed for iAs determination by the HG-HR-CS-QTAAS method using extraction in 0.28 mol L^{-1} HNO_3 and 0.01 mol L^{-1} HCl without separation

	Na	K	Mg	Ca	Al	Fe	Cr	Mn	Co	Ni	Cu	Zn	Sr	Ba	Cd	Pb
	Extraction in 0.28 mol L^{-1} HNO_3 without separation															
Min	3.4	0.20	0.30	0.04	0.02	0.04	<0.01	<0.002	<0.02	<0.02	0.05	0.02	<0.007	<0.0004	<0.001	<0.01
Max	160	5.5	2.1	2.5	0.30	0.80	<0.01	<0.002	<0.02	<0.02	0.21	0.90	<0.007	<0.0004	<0.001	<0.01
Mean	51	2.3	1.0	0.70	0.15	0.30	<0.01	<0.002	<0.02	<0.02	0.13	0.20	<0.007	<0.0004	<0.001	<0.01
SD	30	1.7	0.70	0.50	0.09	0.20	<0.01	<0.002	<0.02	<0.02	0.06	0.13	<0.007	<0.0004	<0.001	<0.01
	Extraction in 0.01 mol L^{-1} HCl without separation															
Min	0.70	0.03	0.07	0.06	0.08	0.08	<0.01	<0.002	<0.02	<0.02	0.02	0.02	<0.007	<0.0004	<0.001	<0.01
Max	10.0	4.2	2.3	0.70	0.40	0.40	<0.01	<0.002	<0.02	<0.02	0.04	0.50	<0.007	<0.0004	<0.001	<0.01
Mean	3.1	1.7	0.5	0.30	0.20	0.20	<0.01	<0.002	<0.02	<0.02	0.03	0.20	<0.007	<0.0004	<0.001	<0.01
SD	2.5	1.3	0.2	0.20	0.10	0.10	<0.01	<0.002	<0.02	<0.02	0.02	0.10	<0.007	<0.0004	<0.001	<0.01

7. Comparison of measurement results with the certified or reference values obtained by the Dunnett's method

Table S7. Significant differences ($p < 0.05$) between the found means and certified/reference means in CRMs using the Dunnett's method

CRM	Certified or reference value ± U[a] (mg kg^{-1})	Calib. Method	Significant differences for recovery (mean ± U_{lab})[b] (%)					
			Extraction in 10 mol L^{-1} HCl			Extraction in 0.28 mol L^{-1} HNO_3	Extraction in 0.01 mol L^{-1} HCl	Pooled results
			IMEP-41 procedure[c]	Separation by extraction in toluene[d]	Without separation[d]	Without separation[d]	Without separation[d]	
ERM – BC211 Rice	0.124 ± 0.011	Ext.						
		Std. Ad.						
ERM – CE278k Mussel tissue	0.086 ± 0.008[e]	Ext.						
		Std. Ad.						
	0.133 ± 0.048[e]	Ext.	0.00020	0.00010	0.000606	0.014565	0.000417	0.000246
		Std. Ad.	0.00016	0.00010	0.014565	0.003749	0.003749	0.000246
BCR – 627 Tuna fish tissue	0.063 ± 0.027[e]	Ext.						
		Std. Ad.						
SRM 2976 Mussel Tissue	0.110 ± 0.013[f]	Ext.						
		Std. Ad.						
IAEA-359 Cabbage	0.091 ± 0.016[e]	Ext.						
		Std. Ad.						
	0.074 ± 0.033[e]	Ext.					0.001056	
		Std. Ad.		0.009675			0.002262	
Tort-2 Lobster Hepatopancreas	0.71 ± 0.04[f]	Ext.	0.021330	0.018234				
		Std. Ad.	0.013476	0.027208		0.048806		
	0.582 ± 0.081[g]	Ext.						
		Std. Ad.						
	0.615 ± 0.086[g]	Ext.						
		Std. Ad.						
	0.544 ± 0.162[h]	Ext.						
		Std. Ad.						

[a] U is the expanded uncertainty (k = 2, 95% confidence level); [b] U_{lab} – is the expanded uncertainty in laboratory (k = 2, n = 5 parallel measurements and 95% confidence level; [c] IMEP-41 procedure, prereduction with HBr and hydrazine sulfate, separation of iAs in toluene-1 mol L^{-1} HCl system, derivatization to arsine with $NaBH_4$ in 1 mol L^{-1} HCl[25,53]; [d] prereduction with L-cysteine and derivatization to arsine with $NaBH_4$ in 0.01 mol L^{-1} HCl and 0.2% L-cysteine; [e] reference values from[4,25,53]; [f] reference values from[59]; [g] reference values calculated as mean according to the results centralized by Petursdottir *et al.*[3,13,33]; [h] reference values from[52]

Table S8. Recovery of iAs in CRMs against certified value (ERM-BC211 Rice) and reference values from literature

CRM	Certified or reference value ± U[a] (mg kg^{-1})	Calib. method	Recovery (mean ± U_{lab})[b] (%) Extraction in 10 mol L^{-1} HCl			Extraction in 0.28 mol L^{-1} HNO_3	Extraction in 0.01 mol L^{-1} HCl	Pooled results
			IMEP-41 procedure[c]	Separation by extraction in toluene[d]	Without separation[d]	Without separation[d]	Without separation[d]	
ERM - BC211 Rice	0.124 ± 0.011	Ext.	98 ± 20	94 ± 20	97 ± 13	94 ± 19	101 ± 30	97 ± 21
		Std. Ad.	106 ± 15	92 ± 22	101 ± 21	92 ± 22	94 ± 38	97 ± 25
ERM - CE278k Mussel tissue	0.086 ± 0.008[e]	Ext.	100 ± 10	94 ± 31	112 ± 17	122 ± 25	110 ± 27	108 ± 23
		Std. Ad.	99 ± 15	93 ± 33	122 ± 24	117 ± 33	117 ± 28	110 ± 27
	0.133 ± 0.048[e]	Ext.	**65 ± 10[j]**	**61 ± 31[j]**	**72 ± 17[j]**	**79 ± 25[j]**	**71 ± 27[j]**	-
		Std. Ad.	**64 ± 15[j]**	**60 ± 33[j]**	**79 ± 24[j]**	**76 ± 33[j]**	**86 ± 28[j]**	-
BCR - 627 Tuna fish tissue	0.063 ± 0.027[e]	Ext.	86 ± 26	86 ± 26	103 ± 22	87 ± 18	103 ± 12	93 ± 21
		Std. Ad.	90 ± 19	86 ± 20	108 ± 21	103 ± 29	98 ± 24	97 ± 23
SRM 2976 Mussel Tissue	0.110 ± 0.013[f]	Ext.	92 ± 36	87 ± 35	100 ± 27	96 ± 28	99 ± 28	95 ± 31
		Std. Ad.	89 ± 23	102 ± 28	95 ± 18	93 ± 14	94 ± 12	95 ± 20
IAEA-359 Cabbage	0.091 ± 0.016[e]	Ext.	101 ± 22	96 ± 21	**89 ± 35[i]**	97 ± 19	**119 ± 26[i]**	103 ± 22
		Std. Ad.	93 ± 31	112 ± 27	93 ± 31	101 ± 27	116 ± 26	103 ± 28
	0.074 ± 0.033[e]	Ext.	124 ± 22	118 ± 21	109 ± 20	119 ± 19	**146 ± 26[j]**	123 ± 22
		Std. Ad.	115 ± 31	**138 ± 27[j]**	115 ± 31	124 ± 27	**143 ± 26[j]**	127 ± 28
Tort-2 Lobster Hepatopancreas	0.71 ± 0.04[f]	Ext.	**71 ± 18[j]**	**70 ± 23[j]**	92 ± 21	87 ± 20	87 ± 22	89 ± 21
		Std. Ad.	**69 ± 24[j]**	**72 ± 18[j]**	87 ± 19	**74 ± 31[j]**	86 ± 21	87 ± 20
	0.582 ± 0.081[g]	Ext.	87 ± 18	86 ± 23	113 ± 21	106 ± 20	107 ± 22	100 ± 21
		Std. Ad.	85 ± 24	88 ± 18	106 ± 19	90 ± 31	105 ± 21	95 ± 23
	0.615 ± 0.086[g]	Ext.	82 ± 18	81 ± 23	107 ± 21	100 ± 20	101 ± 22	94 ± 21
		Std. Ad.	80 ± 24	83 ± 18	100 ± 19	85 ± 31	99 ± 21	89 ± 23
	0.544 ± 0.162[h]	Ext.	93 ± 18	92 ± 23	120 ± 21	113 ± 20	114 ± 22	106 ± 21
		Std. Ad.	91 ± 24	94 ± 18	113 ± 19	97 ± 31	112 ± 21	101 ± 23
Pooled recovery (%)		Ext.	92 ± 22	90 ± 26	107 ± 19	102 ± 21	107 ± 24	100 ± 23
		Std. Ad.	92 ± 22	94 ± 24	105 ± 22	97 ± 28	104 ± 25	98 ± 24

[a] U is the expanded uncertainty (k = 2, 95% confidence level); [b] U_{lab} – is the expanded uncertainty in laboratory (k = 2, n = 5 parallel measurements and 95% confidence level; [c] IMEP-41 procedure, prereduction with HBr and hydrazine sulfate, separation of iAs in toluene-1 mol L^{-1} HCl system, derivatization to arsine with $NaBH_4$ in 1 mol L^{-1} HCl[25,53]; [d] prereduction with L-cysteine and derivatization to arsine with $NaBH_4$ in 0.01 mol L^{-1} HCl and 0.2% L-cysteine; [e] reference values from[4,25,53]; [f] reference values from[59]; [g] reference values calculated as mean according to the results centralized by Petursdottir *et al.*[3,13,33]; [h] reference values from[52]; [i]significant differences ($p < 0.05$) using Tukey's method; [j]significant differences ($p < 0.05$) against certified/reference values using Dunnett's method

8. Weight of iAs fractions in foodstuffs

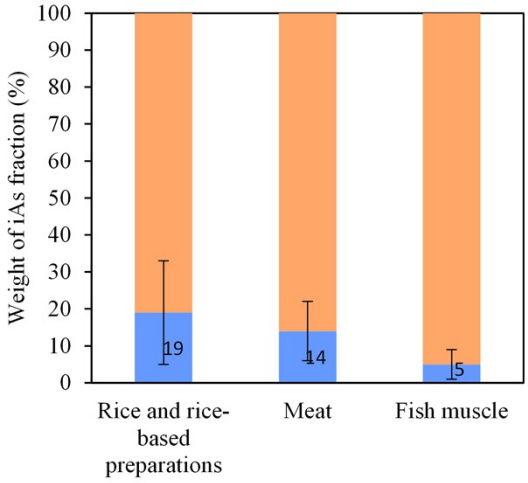

Fig. S9. Weight of iAs fraction (blue column) from total in foodstuffs

Author contributions

Lucia Chirita: Investigation, Methodology, Resources, Funding acquisition, Data curation, Formal analysis, Writing – original draft. **Eniko Covaci**: Formal analysis, Visualization, Data curation, Software, Writing – original draft. **Michaela Ponta**: Validation, Writing – original draft. **Tiberiu Frentiu**: Conceptualization, Supervision, Funding acquisition, Project administration, Writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by a grant of Ministry of Research and Innovation, Romania, project CNFIS-FDI-2022-0179, within PNCDI III and project financed by the European Commission, number POCU/380/6/13/123886.