

Electronic Supplementary Information

Mercury determination in various environmental, food and material complex matrices using unified operation conditions for cold vapor generation high-resolution continuum source quartz tube atomic absorption spectrometry method

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1. Mercury toxicity and the current legislation on protecting the environment and food against contamination

Mercury as elemental (Hg^0), inorganic (Hg^{2+}) and organic (methylmercury - CH_3Hg^+ , ethylmercury - $\text{C}_2\text{H}_5\text{Hg}^+$ and phenylmercury - $\text{C}_6\text{H}_5\text{Hg}^+$) species are harmful for natural ecosystem and human health as a result of accumulation in various environmental compartments (soil, water sediment, plants, etc.) and biological tissue with disastrous effect on the central nervous system.^{1–8} Thus, the Hg level is regulated in national and international legislation, namely at 0.5 mg kg^{-1} in freshwater fish species and 1 mg kg^{-1} in seafood set in European Commission Regulation 1881/2006/EC, $50 \text{ } \mu\text{g L}^{-1}$ in surface water in Directive 2008/105/EC and $1 \text{ } \mu\text{g L}^{-1}$ in mineral water in *Codex Alimentarius*.^{9–11} World Health Organization and United Nations Environment Programme mention a value of $10 \text{ } \mu\text{g L}^{-1}$ in

blood.¹² The concentration is usually below $10 \mu\text{g kg}^{-1}$ in foods of animal and vegetable origin in which Hg is not regulated.¹³ Mercury is included in the list of priority hazardous substances in Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment.¹⁴ Since the risk of Hg contamination is a worldwide problem, several international conventions have been ratified, the most prominent being the Minamata Convention adopted in 2013 and subsequently ratified by 140 states between 2013–2018.¹⁵ The Minamata Convention is a global legal framework establishing actions aiming at reducing global Hg pollution, as well as the need to monitor Hg and its species in the environment for an accurate assessment of pollution level and identification of population at risk. According to this Convention, the European Parliament and the Council adopted the Regulation 852/2017/EU on mercury concerning measures that should be taken by the member states to reduce considerably the exposure risk from anthropogenic activities, since between 40 and 80% of total Hg in the European Union originates from outside.¹⁶

2. CVG-HR-CS-QTAAS instrumentation using HS55-manual system and operating procedure

The experimental set-up is illustrated in Fig. S1.

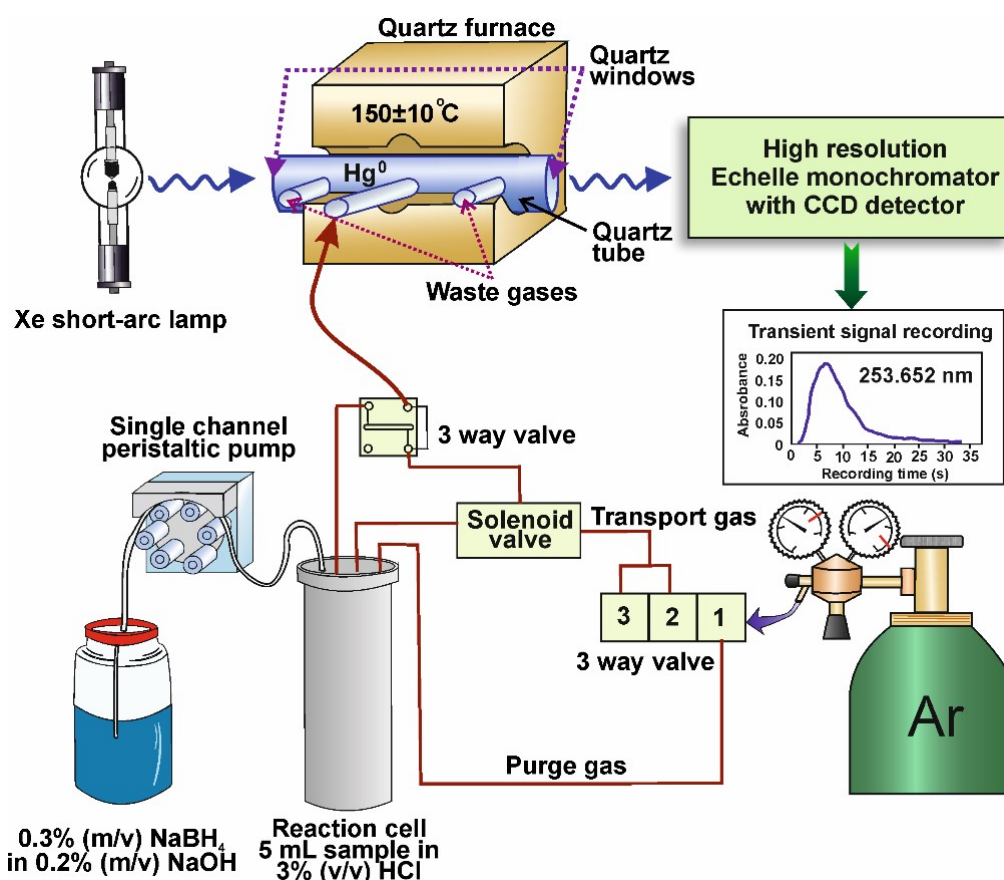


Fig. S1. The experimental set-up CVG-HR-CS-QTAAS equipped with HS55-manual system

The ContrAA 300 Spectrometer is equipped with a high-intensity xenon short-arc lamp with continuum emission in the range 190–900 nm, a high-resolution double monochromator 2 pm Full Width at Half Maximum (FWHM) and a charge coupled device (CCD) detector with 512 pixels, 200 of which were used for recording the absorption spectrum in the range ± 0.1 nm of Hg 253.652 nm analytical line. A number of 5 pixels in the middle of the spectral window were assigned to measure absorption signal of Hg, while the other pixels were used to background measurement. A background correction was performed by subtracting the background spectrum of a 3% (v/v) HCl blank solution from the total absorption at the Hg line. The HS55-manual system encompassed a PTFE reaction cell, a single-channel peristaltic pump for introduction of NaBH₄ solution and a set of three-way valves to control the Ar flow for purging and transporting cold vapor to the quartz tube cell. The quartz tube has a length of 140 mm and an i.d. of 15 mm with end windows and is mounted in an electric furnace, which ensure a temperature of 150 ± 10 °C needed for water droplets evaporation entrained from the reaction cell, and thus, the elimination of radiation dispersion by the droplets.

The operating procedure consisted in manually pipetting an aliquot volume of 5 mL standard/sample solution in the reaction cell and delivering of 3.5 mL NaBH₄ solution *via* the peristaltic pump. Mercury vapor generated in the cell was transported by a 6 L h⁻¹ Ar stream to the quartz tube, where Hg atoms absorbed the radiation of 253.652 nm from the Xe lamp. The CCD detector does not allow real-time measurements, so episode absorption spectra were recorded and the corresponding transient signal of Hg at 253.652 nm was registered over up to 60 s. Optimization of CVG conditions was obtained using both peak height and area measurement of the transient signal using ASpects CS 2.2.1, Analytik Jena, software. Then, the measurements in the current study were performed using peak height mode for which the maximum of transient signal was reached after 20 s.

3. Influence of the chemical parameters on the CVG process

Fig. S2 reveals a significant influence of HCl concentration on CVG from Hg²⁺ species with an optimal value of 3% (v/v) HCl in both measurement modes. Since the instrument software does not allow adjustment of the Ar flow rate, all determinations were performed at a flow rate of 6 L h⁻¹. For NaBH₄ (Fig. S3) and NaOH (Fig. S4) solutions the optimal values were found to be 0.3% (m/v) and 0.2% (m/v), respectively. The decrease of the signal at concentrations higher than 3% HCl and 0.3% NaBH₄ is due to the additional volume of hydrogen generated and the dilution of Hg cold vapor from the path of the optical beam in the quartz tube. Also, at concentrations higher than 0.2% NaOH, the efficiency of derivatization to CV of Hg²⁺ ions decrease by neutralizing the HCl in the sample.

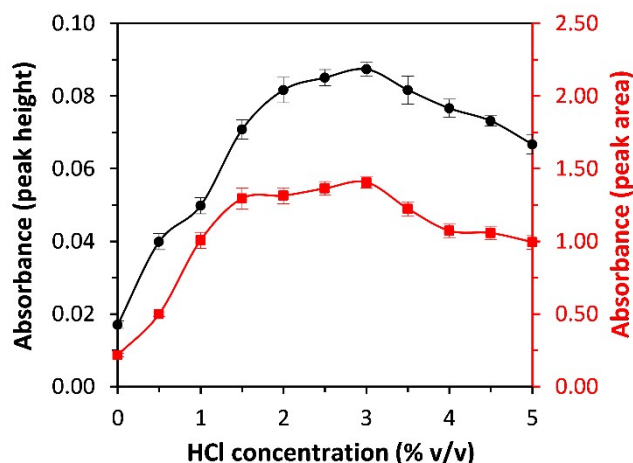


Fig. S2. Influence of HCl concentration on CVG from aliquot volumes of 5 mL standard solution containing $5 \mu\text{g L}^{-1} \text{Hg}^{2+}$ in peak height and peak area measurement of absorption transient signal. Volume of 0.3% NaBH_4 in 0.2% NaOH : 3.5 mL for peak height and 5 mL for peak area. Error bars correspond to standard deviation ($n = 5$)

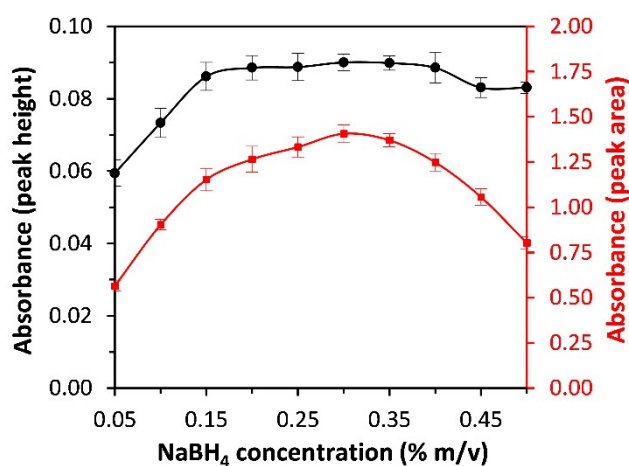


Fig. S3. Influence of NaBH_4 concentration in 0.2% (m/v) NaOH on CVG from aliquot volumes of 5 mL standard solution containing $5 \mu\text{g L}^{-1} \text{Hg}^{2+}$ in 3% (v/v) HCl in peak height and peak area measurement of absorption transient signal. Volume of 0.3% NaBH_4 in 0.2% NaOH : 3.5 mL for peak height and 5 mL for peak area. Error bars correspond to standard deviation ($n = 5$)

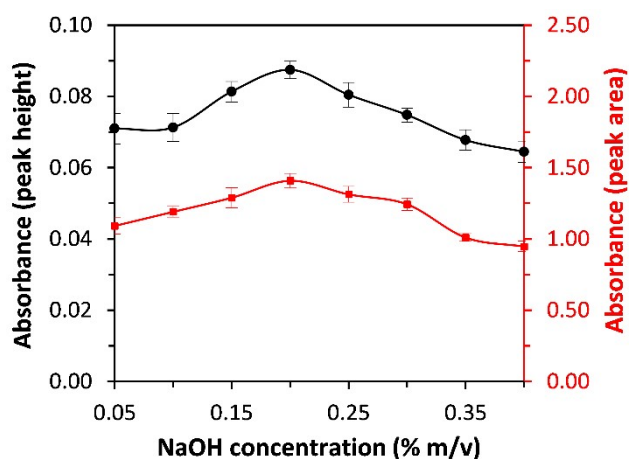


Fig. S4. Influence of NaOH concentration for 0.3% (m/v) NaBH₄ on CVG from aliquot volumes of 5 mL standard solution containing 5 μg L⁻¹ Hg²⁺ in peak height and peak area measurement of absorption transient signal. Volume of 0.3% NaBH₄ in 0.2% NaOH: 3.5 mL for peak height and 5 mL for peak area. Error bars correspond to standard deviation (n = 5)

It was also observed a relationship between the absorption response and volume of NaBH₄ solution added to the sample, so that the behavior of the absorption signal was studied for volumes of NaBH₄ in the range 1.5–6 mL added over the aliquots of 5 mL standard containing Hg²⁺. Results are presented in Fig. S5.

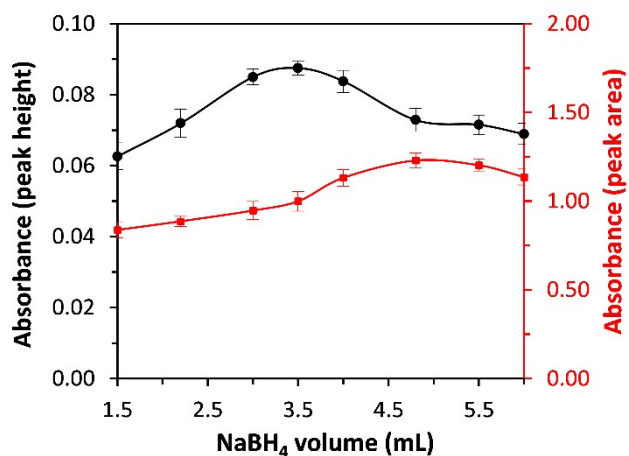


Fig. S5. Influence of the volume of 0.3% (m/v) NaBH₄ in 0.2% (m/v) NaOH on the CVG from aliquot volumes of 5 mL standard solution containing 5 μg L⁻¹ Hg²⁺ in 3% (v/v) HCl in peak height and peak area measurement of absorption transient signal. Error bars correspond to standard deviation (n = 5)

The curves in Fig. S5 show that the volume of the NaBH₄ derivatization solution is crucial for the magnitude of absorption response as it influences the derivatization yield. Moreover, distinct optimal volumes of 0.3% NaBH₄ in 0.2% NaOH were found for the two measurement modes, namely 3.5 mL (peak height) and 5 mL (peak area).

The quartz end windows prevented air diffusion into the quartz tube and provided an inert atmosphere of Ar resulting in a significant decrease of continuum background in the vicinity of Hg 253.652 nm line. The recording of the Hg signal was performed after 20 s from the auto zero signal adjustment, after which the volume of 3.5 mL of NaBH₄ solution was introduced by pumping for 13 s. The mercury vapor purge time was 20 s. The cross memory effects were avoided by additionally purging the reaction cell and the quartz tube for 20 s after recording the Hg analytical signal. These ensured a very good repeatability and reproducibility of the analytical signal and background, respectively, with a positive influence on the figures of merit of the CVG-HR-CS-QTAAS method.

4. Influence of number of pixels associated to Hg 253.652 nm analytical line on analytical performance

Table S1. Influence of number of pixels associated to Hg 253.652 nm analytical line on analytical performance

| Nr. of pixels | Calibration curve parameters | | | CRM BCR 463 Tuna fish analysis | | | | |
|---------------|------------------------------|----------------------------------|----------------|-------------------------------------|---|---|---|------------------------------------|
| | Intercept | Slope (L μg^{-1}) | R ² | Analytical sensitivity ^a | Certified value $\pm U_{\text{CRM}}^{\text{b}}$ (mg kg ⁻¹) | Found value $\pm U_{\text{lab}}^{\text{c}}$ (mg kg ⁻¹) | Accuracy ^d R $\pm U_{\text{lab}}(\%)$ | Precision RSD($\%)^{\text{e}}$ |
| 1 | -0.0001 | 0.0050 | 0.9989 | 94 | 2.85 \pm 0.16 | 2.97 \pm 0.71 | 104 \pm 24 | 11.1 |
| 3 | 0.0004 | 0.0127 | 0.9996 | 146 | | 3.06 \pm 0.61 | 107 \pm 20 | 8.5 |
| 5 | 0.0004 | 0.0170 | 0.9998 | 225 | | 3.00 \pm 0.52 | 105 \pm 17 | 6.3 |
| 7 | 0.0007 | 0.0201 | 0.9997 | 191 | | 3.08 \pm 0.58 | 108 \pm 19 | 6.8 |

^a Ratio between calibration sensitivity (slope) and standard deviation of the slope, corresponding to the signal-to-noise ratio for 1 $\mu\text{g L}^{-1}$ Hg

^b U_{CRM} is expanded uncertainty for certified concentration (k = 2; 95% confidence level).

^c U_{lab} is expanded uncertainty in laboratory (k = 2, n = 5 parallel measurements and 95% confidence level).

^d R is the recovery expressed in %.

^e RSD is the relative standard deviation for n = 5 parallel measurements and 95% confidence level.

5. Comparison of analytical performance for Hg determination by CVG-HR-CS-QTAAS with other methods

Table S2. Limit of detection, recovery and precision of Hg determination by CVG-HR-CS-QTAAS and other methods in different matrices in which the maximum level of Hg has been set.

| Method ^a | Matrices | Hg species | Preparation procedure | LOD | Recovery(%) | Precision RSD(%) | Reference ^b |
|---------------------|--|------------|--|---|-------------|------------------|------------------------|
| CVG-HR-CS-QTAAS | Seafood, soil, water sediment and sludge | Total Hg | Digestion and batch derivatization without preconcentration | 0.014 ± 0.001 mg kg ⁻¹ | 93–107 | 4.2–15.0 | This paper |
| | Water | Total Hg | Dilution | 0.064 ± 0.004 µg L ⁻¹ | 103 ± 16 | - | This paper |
| | (Bio)polymeric materials | Total Hg | Digestion and batch derivatization without preconcentration | 0.009 ± 0.001 mg kg ⁻¹ | 98–99 | 6.5–15.0 | This paper |
| HR-CS-GFAAS | Soil and sludge | Total Hg | <i>Aqua regia</i> microwave digestion; <i>aqua regia</i> leaching; slurry; preconcentration by amalgamation on AuPNs/PdNPs | 0.9/0.3 mg kg ⁻¹ ; 0.2/0.7 mg kg ⁻¹ ; 1.3/0.6 mg kg ⁻¹ | 99–100 | 0.9–4.1 | 32 |
| CV-ICP-MS | Marine sediment, Marine biota, Sea water | Total Hg | Acid microwave-assisted digestion and CV generation with SnCl ₂ | 0.00072 µg L ⁻¹ | 97–103 | 1.9–3.7 | 11 |
| UV-PVG-ICP-OES | Wastewater Estuarine sediment | Total Hg | Photochemical cold vapor generation with 15% (v/v) formic acid | 0.090 µg L ⁻¹ | 89–97 | - | 8 |
| HR-CS-GFAAS | Phosphate fertilizer | Total Hg | Direct solid sampling | 0.0048 mg kg ⁻¹ | 103 ± 4 | 4.4–8.2 | 31 |
| HR-CS- | Water | Total Hg | USA-DMSPE on AgNPs as solid sorbent and leaching in 7 mol L ⁻¹ HNO ₃ | 0.005 µg L ⁻¹ | 96–104 | 6–11 | 33 |

ETAAS

| | | | | | | | |
|-------------------------|-------------------------------------|--|--|--|-------------|---------|----|
| CV-HR-CS-ETAAS | Water | Total Hg | Preconcentration by chelating on DPTH-MNPs | 0.22 $\mu\text{g L}^{-1}$ | 90–110 | 2.2–2.9 | 35 |
| FI-SPE-CVG-HR-CS-ETAAS | Water | Total Hg | On line preconcentration by chelating on silica functionalized with DPTH and CVG derivatization with NaBH_4 | 0.17 $\mu\text{g L}^{-1}$ | 91–103 | 1.9–2.4 | 36 |
| HR-CS-GFAAS | Biological fluids (blood and urine) | Total Hg | Direct determination and AuNPs as chemical modifier | 2.3 $\mu\text{g L}^{-1}$ | 83–104 | 10–15 | 34 |
| CV-AFS | Fish muscle | Total Hg | Acid MAWD in $\text{HNO}_3 + \text{H}_2\text{O}_2$ mixture and CV generation with SnCl_2 | 0.012 $\mu\text{g L}^{-1}$ | 97 \pm 7 | 0.8–7.7 | 7 |
| TD-AAS | Fish muscle | Total Hg | Direct solid sampling | 0.010 mg kg^{-1} | 100 \pm 3 | 1.8–5.5 | 38 |
| HPLC-UV-CV-AFS | Seafood, yeast and garlic | Speciation (Hg^{2+} ; CH_3Hg^+ ; $\text{C}_2\text{H}_5\text{Hg}^+$) | Separation on C-18 column and post column UV-CV derivatization | 0.05–0.11 $\mu\text{g L}^{-1}$ | 96–100 | 2 | 19 |
| HPLC-UV-PVG-HR-CS-QTAAS | Fish muscle | Speciation (Hg^{2+} ; CH_3Hg^+ ; $\text{C}_2\text{H}_5\text{Hg}^+$; $\text{C}_6\text{H}_5\text{Hg}^+$) | Extraction in TMAH or HCl at 75 °C | 0.47; 0.84; 0.80; 2 $\mu\text{g L}^{-1}$ | 82–83 | 3.6 | 37 |
| LA-ICP-MS | Plastics | Total Hg | Direct solid sampling | 1 mg kg^{-1} | 166 | 40 | 56 |
| CV-ICP-MS | Plastics | Total Hg | MAWD in $\text{HNO}_3 + \text{HCl}$ mixture and CV generation | 0.054 mg kg^{-1} | - | - | 57 |
| CV-ICP-MS | Plastics | Total Hg | MAWD-SRC in $\text{HNO}_3 + \text{HCl}$ mixture and CV generation | 0.029 mg kg^{-1} | 102 | 3.8 | 57 |
| CV-ICP-MS | Plastics | Total Hg | MIC, absorption in $\text{HNO}_3 + \text{HCl}$ mixture and CV generation | 0.011 mg kg^{-1} | 102 | 8.4 | 58 |

^a HR-CS-GFAAS – high-resolution continuum source graphite furnace atomic absorption spectrometry; HR-CS-ETAAS – high-resolution continuum source electrothermal atomic absorption spectrometry; CV-HR-CS-ETAAS – cold vapor high-resolution continuum source electrothermal atomic absorption spectrometry; FI-SPE-CVG-HR-CS-ETAAS – flow injection solid-phase extraction high-resolution continuum source electrothermal atomic absorption spectrometry; CV-AFS – cold vapor atomic fluorescence spectrometry; CV-ICP-MS – cold vapor inductively coupled plasma mass spectrometry; UV-PVG-ICP-OES – ultraviolet photo-induced vapor generation inductively coupled plasma optical emission spectrometry; TD-AAS – thermal desorption atomic absorption spectrometry; HPLC-UV-CV-AFS – high-performance liquid chromatography ultraviolet cold vapor atomic fluorescence spectrometry; HPLC-UV-PVG-HR-CS-QTAAS – high-performance liquid chromatography ultraviolet photo-induced vapor generation high-resolution continuum source quartz tube atomic absorption spectrometry; USA-DMSPE – ultrasound-assisted dispersive micro solid-phase extraction; DPTH-MNPs – magnetic solid phase extraction using 1,5 bis(di-2-pyridyl) methylene thiocarbohydrate; TMAH – tetramethylammonium hydroxide; MAWD – microwave-assisted wet digestion; MAWD-SRC – microwave-assisted wet digestion in single reaction chamber; MIC – microwave-induced combustion.

^b References from this table are those indicated in the main paper.

6. Composition of the multielement matrix for CRMs and real test samples analyzed for Hg determination by CVG-HR-CS-QTAAS

Table S3. Composition of the multielement matrix determined by HR-CS-FAAS of samples analyzed that did not have non-spectral effects in the determination of mercury by CVG-HR-CS-QTAAS

| Value | Element concentration (mg L ⁻¹) | | | | | | | | | | | | | | | |
|--|---|-------|-------|-------|------|-------|-------|-------|-------------------|-------|-------|-------|-------|------|-------|------|
| CRM of fish, mussel tissue and mushroom | | | | | | | | | | | | | | | | |
| | Na | K | Mg | Ca | Al | Fe | Cr | Mn | Co | Ni | Cu | Zn | Sr | Ba | Cd | Pb |
| Min. | 0.8 | 1.5 | 0.2 | 0.1 | 0.01 | 0.01 | 0.1 | 0.004 | <LOD ^a | 0.001 | 0.002 | 0.02 | 0.02 | <LOD | 0.004 | 0.01 |
| Max. | 1179 | 300 | 98 | 154 | 3.1 | 4.4 | 0.5 | 0.6 | <LOD | 0.2 | 0.9 | 4.0 | 1.7 | <LOD | 0.2 | 0.2 |
| Mean | 165 | 51 | 14 | 24 | 0.6 | 0.8 | 0.2 | 0.2 | <LOD | 0.05 | 0.1 | 0.7 | 0.5 | <LOD | 0.1 | 0.04 |
| St. Dev. | 364 | 92 | 30 | 48 | 1.1 | 1.4 | 0.2 | 0.2 | <LOD | 0.1 | 0.3 | 1.3 | 0.7 | <LOD | 0.1 | 0.06 |
| CRM of wastewater, water sediment and soil | | | | | | | | | | | | | | | | |
| Min. | 0.001 | 0.003 | 0.001 | 0.015 | 0.01 | 0.009 | 0.004 | 0.02 | 0.004 | 0.01 | 0.003 | 0.005 | 0.005 | 0.02 | 0.003 | 0.03 |
| Max. | 5.3 | 21 | 17 | 41 | 341 | 41 | 0.2 | 1.7 | 40 | 0.1 | 0.4 | 1.7 | 0.1 | 1.1 | 0.3 | 0.2 |
| Mean | 0.6 | 3.6 | 2.3 | 7.4 | 40 | 9.8 | 0.05 | 0.3 | 12 | 0.03 | 0.1 | 0.4 | 0.02 | 0.2 | 0.1 | 0.1 |
| St. Dev. | 1.5 | 7.4 | 4.9 | 14 | 102 | 16 | 0.05 | 0.6 | 18 | 0.02 | 0.1 | 0.5 | 0.03 | 0.4 | 0.1 | 0.1 |
| Soil test samples | | | | | | | | | | | | | | | | |
| Min. | 0.3 | 0.4 | 0.1 | 4.4 | 2.4 | 6.3 | 0.003 | 0.6 | 0.01 | 0.02 | 0.1 | 0.3 | 0.1 | 0.1 | 0.01 | 0.2 |
| Max. | 950 | 5.2 | 8.9 | 595 | 48 | 28 | 0.10 | 3.2 | 0.1 | 0.1 | 0.3 | 5.0 | 0.5 | 0.5 | 0.2 | 0.6 |
| Mean | 204 | 1.6 | 2.6 | 140 | 11 | 14 | 0.03 | 1.6 | 0.02 | 0.04 | 0.2 | 1.5 | 0.3 | 0.2 | 0.1 | 0.4 |
| St. dev. | 373 | 1.8 | 3.2 | 212 | 17 | 8 | 0.04 | 1.0 | 0.01 | 0.03 | 0.1 | 1.6 | 0.2 | 0.1 | 0.1 | 0.2 |
| Water sediment and sludge test samples | | | | | | | | | | | | | | | | |
| Min. | 0.2 | 1.3 | 1.3 | 2.4 | 0.04 | 8.7 | 0.1 | 0.2 | <LOD | 0.03 | 0.1 | 0.2 | <LOD | <LOD | <LOD | 0.01 |
| Max. | 12 | 20 | 38 | 25 | 10.3 | 166 | 0.3 | 3.5 | <LOD | 0.10 | 0.5 | 4.1 | <LOD | <LOD | <LOD | 0.04 |
| Mean | 2.7 | 6.4 | 11 | 11 | 2.5 | 57 | 0.2 | 1.4 | <LOD | 0.06 | 0.2 | 1.1 | <LOD | <LOD | <LOD | 0.03 |
| St. dev. | 3.4 | 5.1 | 11 | 7.2 | 10 | 49 | 0.1 | 1.3 | <LOD | 0.03 | 0.1 | 1.1 | <LOD | <LOD | <LOD | 0.01 |
| Fish and mushroom test samples | | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | | | |
|----------|-----|-----|-----|-----|------|-----|-------|-------|-------|------|------|-----|------|------|------|------|
| Min. | 3.0 | 8.1 | 1.2 | 1.6 | 0.03 | 0.1 | 0.002 | 0.004 | 0.005 | 0.09 | 0.08 | 0.4 | 0.01 | 0.02 | 0.02 | 0.02 |
| Max. | 20 | 45 | 5.8 | 139 | 0.2 | 1.8 | 0.5 | 0.2 | 0.08 | 0.3 | 0.8 | 2.1 | 0.2 | 0.03 | 0.2 | 0.2 |
| Mean | 8.2 | 24 | 3.0 | 24 | 0.1 | 1.4 | 0.1 | 0.1 | 0.02 | 0.2 | 0.3 | 1.0 | 0.1 | 0.02 | 0.1 | 0.1 |
| St. Dev. | 5.0 | 12 | 1.3 | 43 | 0.1 | 0.6 | 0.2 | 0.1 | 0.02 | 0.1 | 0.2 | 0.6 | 0.06 | 0.02 | 0.1 | 0.05 |

CRM of PE and (bio)polymeric materials (Polyethylene Terephthalate; Polyethylene; Acrylonitrile Butadiene Styrene from computer components and garden tools)

| | | | | | | | | | | | | | | | | |
|----------|-----|-----|-----|-----|-------|------|------|-------|------|------|-----|------|------|------|------|-----|
| Min. | 0.1 | 0.2 | 0.1 | 0.1 | 0.035 | 0.03 | <LOD | 0.007 | <LOD | <LOD | 24 | 0.02 | <LOD | <LOD | 0.01 | 0.2 |
| Max. | 2.3 | 1.6 | 16 | 49 | 0.088 | 19 | <LOD | 0.02 | <LOD | <LOD | 136 | 0.8 | <LOD | <LOD | 0.06 | 0.6 |
| Mean | 0.5 | 0.6 | 2.1 | 11 | 0.058 | 2.7 | <LOD | 0.01 | <LOD | <LOD | 68 | 0.2 | <LOD | <LOD | 0.03 | 0.4 |
| St. Dev. | 0.6 | 0.4 | 4.5 | 14 | 0.027 | 6.0 | <LOD | 0.01 | <LOD | <LOD | 48 | 0.2 | <LOD | <LOD | 0.02 | 0.2 |

^a LODs obtained by HR-CS-FAAS (mg L⁻¹): Na 0.0007; K 0.0011; Mg 0.0006; Ca 0.007; Al 0.03; Fe 0.009; Cr 0.003; Mn 0.001; Co 0.004; Ni 0.004; Cu 0.003; Zn 0.005; Sr 0.005; Ba 0.01; Cd 0.002; Pb 0.016.

7. Combined uncertainty of the found Hg concentrations in the analyzed matrix samples by CVG-HR-CS-QTAAS method using HS55-manual system

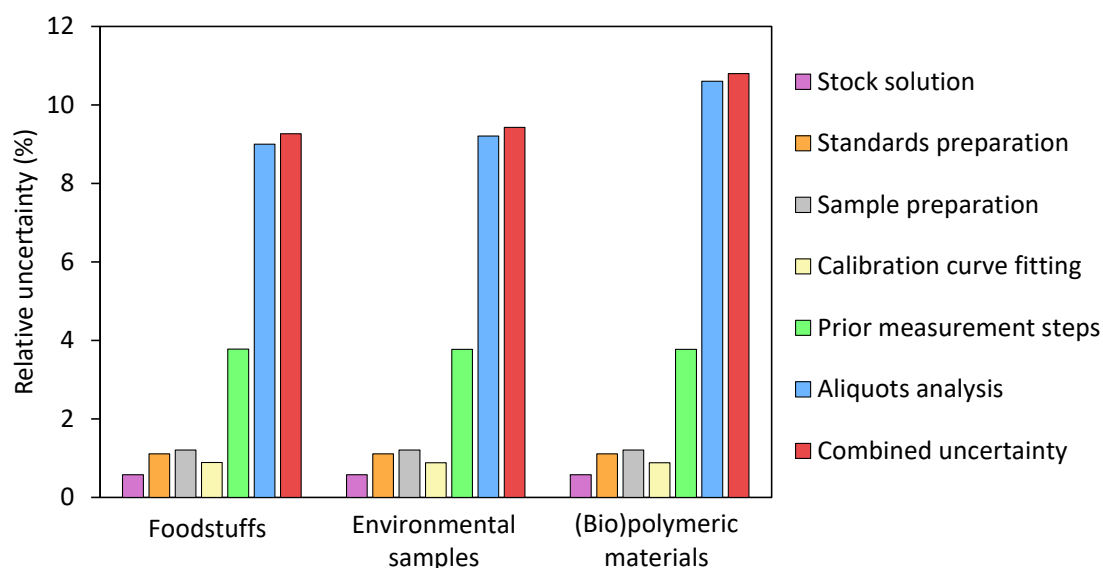


Fig. S6. Combined uncertainty of the found Hg concentrations in the analyzed matrix samples by CVG-HR-CS-QTAAS method using HS55-manual system

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