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# High-resolution continuum source quartz tube atomic absorption spectrometry for the determination of As, Sb, Bi, Hg, Se and Te in food and environmental matrices after chemical vapor generation†

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This study presents a broadly applicable spectrometric method for the determination of As, Sb, Bi, Hg, Se, and Te in food and environmental matrices based on chemical vapor generation high-resolution continuum source quartz tube atomic absorption spectrometry as a sequential method. The samples were subjected to microwave-assisted digestion, followed by the pre-reduction of As(v) and Sb(v) with 0.05 mol $L^{-1}$ thiourea in a 0.5 mol $L^{-1}$ HCl medium and Se(vi) and Te(vi) in a 7 mol $L^{-1}$ HCl medium. Chemical vapor was generated from an aliquot volume of 5 mL sample in 0.5 mol $L^{-1}$ HCl for As, Sb, Bi and Hg and 7 mol $L^{-1}$ for Se and Te by the addition of 3.5 and 2 mL of 2.5% (m/v) $NaBH_4$ solution stabilized in 0.1% (m/v) NaOH for Hg, Se, and Te and As, Bi, and Sb, respectively. Three pretreatment methods, namely, (i) addition of 1% (m/v) sulfamic acid; (ii) $N_2$ purging of the solution for 20 min; and (iii) addition of 1% (m/v) sulfamic acid followed by 10 min $N_2$ purging, were investigated for the elimination of nitrite and $NO_x$ non-spectral interferences in the Se and Te determination. However, it was observed that pre-washing the reaction cell and the quartz tube atomizer with 6 L $min^{-1}$ argon for 20 s (As, Bi, Se, Te) and 30 s (Sb), after sample introduction into the reaction cell and before $NaBH_4$ solution addition, was crucial for the elimination of spectral interferences from residual $NO_x$ and $O_2$, regardless of the sample pretreatment method. An increase in pre-washing time resulted in a decrease in the signal for all elements, indicating that the presence of $O_2$ traces is beneficial for high sensitivity. The limits of detection were (mg $kg^{-1}$) 0.031 (Hg); 0.016 (As); 0.015 (Bi); 0.008 (Sb); 0.084 (Se); and 0.030 (Te). The analysis of certified reference materials indicated recoveries of 98–103% and an expanded uncertainty of ±(17–18)% ($k$ = 2, 95% confidence level). The $z'$ or $z$ scores indicated a satisfactory performance of the method. The precision, evaluated from extended uncertainty ($k$ = 2, $n$ = 3) by analysis of real samples, was in the range of 4–10.7%.

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## Introduction

There is a constant interest in developing methods for sample preparation and fast sequential or simultaneous multi-elemental determination of toxic or essential elements by spectrometric methods in various matrices that are highly sensitive and selective, specifically free from spectral and non-spectral interferences caused by sample concomitants and reagents used in sample preparation.[1–3] Chemical vapor generation (CVG) using $NaBH_4$ as a reducing reagent[4] and more recently UV-photochemical vapor generation (UV-PVG)[5] have emerged as the most widely used methods for the delivery of analytes (As, Sb, Bi, Se, Te, Hg, and several transition metals) to the spectral detector based on atomic absorption spectrometry (AAS),[6,7] atomic fluorescence spectrometry (AFS),[8,9] inductively coupled plasma optical emission or mass spectrometry (ICP-OES/MS),[10–12] or optical emission spectrometry in microplasma sources.[13–19] These methods offer numerous advantages, such as efficient separation of analytes from the sample matrix, high introduction efficiency into the spectral detector and low detection limits. These advantages have rendered them attractive for the analysis of complex matrices, such as food, biological materials, beverages, and environmental samples.[1–3]

The technology based on high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) offers advantages

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over traditional line-source atomic absorption spectrometry (LS AAS) technology due to the improved sensitivity resulting from the use of wavelength-selected absorbance (WSA) or the wavelength-integrated absorbance (WIA).[20–22] Fast sequential multi-elemental analysis and more advanced background and spectral interference correction techniques in the HR-CS AAS have been employed to determine certain chemical vapor-generating elements in the single-element or multi-element methods.[23–29] Unfortunately, although the CVG and UV-PVG methods provide outstanding sensitivity and separation of analytes from the sample matrix, the chemical vapor derivatization procedure remains affected by the non-spectral interferences from nitrate, and especially nitrite anions, resulting from the mixing or non-mixing of $HNO_3$ with HCl and $H_2O_2$ in the digestion and/or derivatization step, regardless of the measurement method, but also from spectral and background interferences from volatile nitrogen oxides, oxygen and water molecules, which significantly affect the determination of As and Se by AAS.[27,30–35] It was shown that nitrite anions and $NO_x$ (strong oxidant) are generated in concentrated mixtures of $HNO_3$ and HCl.[30]

$$NO_3^- + 2H^+ + 2Cl^- \rightarrow NO_2^- + Cl_2 + H_2O \quad (1)$$

$$2NO_3^- + 8H^+ + 6Cl^+ \rightarrow 2NO + 3Cl_2 + 4H_2O \quad (2)$$

$$2NO_2^- + 2H^+ \rightarrow H_2O + NO + NO_2 \quad (3)$$

Nitrite and $NO_x$ have a severe depressive effect on hydride generation and implicitly on the analytical sensitivity.[30] Also, the $NO_x$ traces, which can be purged from the solution and transported together with the analyte to the quartz tube atomizer (QTA) in the hydride generation step, show not only non-spectral interferences in the liquid phase but also severe spectral interferences in the analytical lines of the hydride generating elements, and a high and noisy background signal that compromises the determination.[27,30–35] Several reagents were studied for the chemical decomposition of $NO_2^-$ before derivatization to chemical vapors, of which sulfamic acid proved to be the most efficient.[30–33] It has been demonstrated that the nitrate anion exerts a much lower depressive effect than the nitrite anion, and its decomposition by sulfamic acid proceeds very slowly in comparison with the decomposition of the nitrite anion.[30]

$$NO_3^- + HSO_3NH_2 \rightarrow N_2O + HSO_4^- + H_2O \quad (4)$$

$$NO_2^- + HSO_3NH_2 \rightarrow N_2 + HSO_4^- + H_2O \quad (5)$$

The sensitivity of chemical vapor-generating element determination by CVG-AAS depends on many operating parameters of the atomization cell, such as the diameter of the quartz tube, temperature and composition of the gaseous atmosphere containing the absorbing atoms. It has been shown that excess hydrogen is necessary to favor the atomization of hydrides, but even a trace amount of oxygen, without the need for supplemental addition, has a positive influence on the sensitivity of the determination of CVG elements such as As and Se.[36,37] The atomization of the As and Se hydrides and the behavior of As and Se atoms in heated quartz tubes and dielectric barrier discharge as atomizers have been the subject of many recent studies.[14–17]

The simultaneous multi-elemental determination of CVG elements remains a challenge since there are significant differences between the reagents required for the pre-reduction of the higher oxidation states of As, Sb, Se and Te, and the conditions for derivatization to chemical vapors; consequently, the methods are usually single element or simultaneous multi-elemental under compromised conditions.[10,13] There have been no studies presenting a general method to determine As, Sb, Bi, Hg, Se and Te in various matrices using the chemical vapor generation high-resolution continuum source quartz tube atomic absorption spectrometry (CVG-HR-CS QTAAS). Also, there have been no studies regarding the elimination of spectral interferences caused by the fine structure of the absorption spectrum of $NO_x$ at wavelengths higher than 200 nm ($A^2\Sigma^+ \rightarrow X^2\Pi$, $E_{ex} = 5.45$ eV; 205.28 nm (0,2); 215.49 nm (0,1); 226.94 nm (0,0)) and $O_2$ below 200 nm ($B^3\Sigma_u^- - X^3\Sigma_g^-$ Schumann–Runge transition)[14,16,27,35,38,39] on the analytical lines of the CVG elements. These spectral interferences could be easily highlighted by the CVG-HR-CS QTAAS technology because the spectral environment around the analytical line is displayed in the range of at least ±0.1 nm, a phenomenon that cannot be visualized in the case of the classical LS AAS technology because the measurement is performed only on the tip of the peak. The aim of this study was to develop a sequential multielemental method for the determination of As, Sb, Bi, Hg, Se and Te using the CVG-HR-CS QTAAS under optimum conditions of pre-reduction and classical derivatization to hydrides with $NaBH_4$ from samples in an HCl medium. Also, the elimination of non-spectral interferences in the liquid, primarily from nitrite, and spectral interferences from $NO_x$ and $O_2$, which are present as contaminants in the atomization cell, were also investigated. Several parameters were optimized for the pre-reduction of As(v), Sb(v), Se(vi) and Te(vi). In the case of the As, Sb, Bi, Se and Te determination, the possibility of eliminating spectral interferences and reducing the background noise near the analytical line by the argon pre-washing of the reaction cell and QTA before adding the $NaBH_4$ solution over the acidic sample aliquot was investigated. In the case of Se and Te determination, three methods for the elimination of nitrite and $NO_x$ non-spectral interferences in the liquid phase on CVG by the addition of sulfamic acid, nitrogen purging of the solution, and the combination of sulfamic acid addition-nitrogen purging, all applied after the pre-reduction step, with or without the argon pre-washing of the reaction cell and QTA before adding the $NaBH_4$ solution for the elimination of spectral interferences of $NO_x$ and $O_2$ in the gaseous phase were explored. Following the optimization of the working parameters, which influence the sensitivity of the CVG-HR-CS QTAAS method, the possibility of determining the elements in two groups was investigated, the first consisting of As, Sb, Bi and Hg, and the second consisting of Se and Te. The method was validated in an analytical performance study, in which the limits of detection (LODs), accuracy (recovery and precision) by certified reference

materials (CRMs) analysis, and the applicability on real soil samples, water sediment, sludge, foodstuffs and food supplements were evaluated. In order to facilitate the transfer of the CVG-HR-CS QTAAS method to routine analytical laboratories, commercially available equipment and devices that could be purchased in any laboratory from manufacturers having such instrumentation were used.

## Experimental

### Instrumentation

The experimental determinations were performed using a CVG-HR-CS QTAAS set-up, which includes a high-resolution atomic absorption spectrometer ContrAA 300 (Full Width at Half Maximum, FWHM, 2 pm) (Analytik Jena, Jena, Germany) equipped with a Charge-Coupled Detector (CCD), batch system for chemical vapor generation HS55 that includes a reaction cell, peristaltic pump for adding the $NaBH_4$ solution over the sample aliquot volume from the reaction cell, and a commercial QTA purchased from the spectrometer manufacturer with a length of 140 mm and an inner diameter of 15 mm, as well as quartz windows at each end. A scheme for the CVG-HR-CS QTAAS set-up has already been published.[27] The ContrAA 300 spectrometer equipped with a high-intensity continuous spectrum short-arc xenon lamp (190–900 nm) was used to highlight the absorption spectra for all elements. The absorption spectrum is displayed within the range of ±0.11 to ±0.13 nm (200 pixels) around the analytical line. The analytical signal was obtained using the WIA over 1–9 pixels (CP, CP ± 1, CP ± 2, CP ± 3, CP ± 4) in the center of the spectral window, where CP represents the absorbance measured at the center pixel, while the signal for pixel pairs represents the absorbance at the wings of the absorption line. The signals from the other pixels on both sides of the analytical lines were used for the background correction by subtraction from the WIA signal. This allowed the investigation of the impact of pixel numbers on the slope and linearity of calibration curves. A set of three-way valves regulate the flow rate of Ar for pre-washing the reaction cell and purging the chemical vapor, as well as for its delivery into the QTA heated by an electric oven at 150 ± 10 °C for Hg determination and at 950 ± 10 °C for As, Sb, Bi, Se and Te determination, respectively. Heating the QTA to 150 °C for Hg determination was necessary to evaporate the water droplets and reduce the radiation dispersion within the QTA. The working principle involved the introduction of an aliquot volume of 5 mL acidic sample in the HCl medium into the reaction cell, followed by pre-washing the residual $NO_x$ and $O_2$ from the reaction cell and QTA with Ar at a flow rate of 6 L $h^{-1}$ for 20–60 s in the case of all elements, except for Hg determination. Subsequently, a volume of 1–5 mL $NaBH_4$ solution stabilized in NaOH was introduced over the sample with the peristaltic pump, followed by chemical vapor purging and introduction into the QTA. The signal at the transient peak height was obtained using the WIA procedure. This method ensured a faster analysis in comparison with the signal area integration, as the maximum peak height is registered after 10 s from the start of chemical vapor purging for all elements, in comparison with 15 s for Se, 20 s for Te, and 30 s for As, Bi, Sb and Hg, required for integrating the peak area. In the case of As, Se, Te, Bi and Sb, the reaction cell and QTA pre-washing before the measurement of the analytical signal was necessary due to the spectral interference of $NO_x$ and $O_2$ on the analytical lines and elevated background noise. In the absence of pre-washing, the background correction was compromised, and a lower sensitivity of the method and a negative bias of the results were obtained. The element quantification was based on an 8-point calibration curve (0; 0.1; 0.2; 0.5; 1; 2; 5 and 10 μg $L^{-1}$) in a medium of 0.5 mol $L^{-1}$ HCl and 0.05 mol $L^{-1}$ thiourea for As and Sb, and 7 mol $L^{-1}$ HCl for Se and Te was used for element quantification. The determination of Bi and Hg was performed in 0.5 mol $L^{-1}$ HCl in the absence of thiourea, as the pre-reduction was not necessary.

Analytical performances obtained by the HR-CS QTAAS were compared with those from CVG-ICP-OES using the simultaneous spectrometer Spectro CIROS$^{CCD}$ (Spectro, Kleve, Germany), equipped with a Hydride generation/Cold vapor system HGX-200 (Teledyne CETAC Technologies, Omaha, Nebraska, USA).

The Berghof MWS 3+ system (Berghof, Germany) was used for the microwave-assisted high-pressure digestion of samples.

### Reagents and solutions

Hydrochloric acid 37% (m/m), nitric acid 65% (m/m), hydrogen peroxide 30% (m/m), $NaBH_4$, NaOH (>98%), sulfamic acid and thiourea, all analytical grade, and single element (1000 mg $L^{-1}$) ICP standard solutions of As, Sb, Bi, Hg, Se, and Te stabilized in 0.5 mol $L^{-1}$ $HNO_3$ from Merck (Darmstadt, Germany) were used. A stock solution of 7 mol $L^{-1}$ HCl was prepared as a pre-reducing reagent for Se(VI) and Te(VI) and as a medium for the Se(IV) and Te(IV) derivatization to hydrides. A stock solution of 0.5 mol $L^{-1}$ thiourea was used as a pre-reducing agent of As(V) and Sb(V) to As(III) and Sb(III), respectively. Multi-element solutions of 5 μg $L^{-1}$ As(V) and Sb(V) in 0.5 mol $L^{-1}$ HCl, Se(VI) and Te(VI) in 7 mol $L^{-1}$ HCl were used in the optimization process with respect to pre-reduction and chemical vapor generation. Also, a solution of 5 μg $L^{-1}$ Hg(II) and Bi(III) was employed in the optimization of CVG conditions. Solutions of 0–8 mol $L^{-1}$ HCl were used in the optimization step of Se(VI) and Te(VI) pre-reduction to Se(IV) and Te(IV), whereas 0–0.08 mol $L^{-1}$ thiourea solutions were used for the pre-reduction of As(V) and Sb(V). 1–4% (m/v) $NaBH_4$ solutions stabilized in 0.1–0.4% (m/v) NaOH and 0–8 mol $L^{-1}$ HCl were used to establish the optimal conditions for CVG. A stock solution of 10% (m/v) sulfamic acid was prepared and used to abate nitrite and $NO_x$ interference on the determination of Se and Te. Solutions of 10 μg $L^{-1}$ Se(VI) and Te(VI) in 7 mol $L^{-1}$ HCl and 10% (v/v) $HNO_3$ were prepared for the non-spectral and spectral interference studies of nitrite, $NO_x$ and $O_2$ on the Se (196.027 nm) and Te (214.281 nm) lines in the presence of the added 1% (m/v) sulfamic acid after pre-reduction with and without $N_2$ purging of the solution and pre-washing the reaction cell and QTA with Ar before adding the $NaBH_4$ solution. The spectral interferences of $NO_x$ and $O_2$ on the absorption signals of As (193.696 nm), Sb (217.582 nm) and Bi (223.061 nm) were studied in multi-element solutions of 10 μg $L^{-1}$ in 0.5 mol $L^{-1}$

 

HCl and 0.05 mol $L^{-1}$ thiourea and 10% (v/v) $HNO_3$, using only pre-washing the reaction cell and QTA with Ar before adding the $NaBH_4$ solution. Ultra-pure water (18 MΩ cm) obtained in the laboratory with the purification system (Millipore, Bedford, USA) was used throughout this study.

### Certified reference materials (CRMs) and test samples

The accuracy of the CVG-HR-CS QTAAS method was checked by analyzing several certified reference materials (CRMs), namely, Metranal-32 Light sandy soil, elevated analyte levels, Metranal-34 Loam, elevated analyte levels from Analytika Spol (Vysocany, Czech Republic), CRM025-050 Metals on soil from Resource Technology Corporation (Laramie, USA), ERM-BB422 Fish muscle, ERM-CE278k Mussel tissue, BCR®-185R Bovine liver, ERM®-BB186 Pig kidney (trace elements), ERM-CE464 – total and methylmercury in tuna fish, BCR®-280R Lake sediment (trace elements), ERM-CC580 Estuarine Sediment, from Institute for Reference Materials and Measurements – IRMM (Geel, Belgium), LGC6141 Soil Contaminated with Clinker Ash from Department of Trade and Industry (Teddington Middlesex, UK), SRM 2976 Trace Elements and Methylmercury in Mussel Tissue and SRM® 3280 Multivitamin/Multielement Tablets from National Institute of Standards and Technology (Gaithersburg, USA), CS-M-3 As, Cd, Cr, Cu, Hg, Pb, Se and Zn in Dried Mushroom Powder (*Boletus edulis*) from the Institute of Nuclear Chemistry and Technology (Warsaw, Poland), Tort-2 and Tort-3 Lobster hepatopancreas reference material for Trace Metals from the National Research Council Canada (Ottawa, Ontario Canada), CRM048-50G Trace metals – Sand 1 and SQC001-30G Metals in soil from Sigma-Aldrich (Laramie, USA), GBW10018 Chicken from the Institute of Geophysical and Geochemical Exploration (Langfang, China) and NCS DC78301 River sediment from the China National Center for Iron and Steel (Beijing, China).

The applicability of the CVG-HR-CS QTAAS method was verified by analyzing the samples of different matrices, such as environmental samples (sludge, soil, water sediment) and oral supplements (multivitamins and multi-minerals). The food supplements were purchased from local shops in the city of Cluj-Napoca, Romania, the soil samples were collected from a former non-ferrous (Au, Ag, Cu, Zn and Pb) ore processing plant near the Baia-Mare town (North Romania), while the sludge samples were from a wastewater treatment station.

### CRM and test sample preparation

Several details regarding the sample preparation protocol have already been published.[27,29] Briefly, 0.5 g CRMs, lyophilized test samples of animal or vegetable origin, and oral supplements were digested in the Berghof MWS 3+ microwave digester (Berghof, Germany) in a mixture of 10 mL concentrated $HNO_3$ and 3 mL $H_2O_2$, while those of the sludge, soil and water sediment were digested using 3 mL $HNO_3$ and 9 mL HCl, according to a thermal procedure previously reported.[40,41] After cooling, the digests were made up to 50 mL with ultrapure water and filtered (0.45 μm). In the case of environmental samples with high Si content, HF was not used for complete digestion, as after digestion, it is necessary to neutralize the excess HF with boric acid to protect the QTA and quartz windows. The presence of HF traces in the liquid droplets carried from the reaction cell causes the etching of the walls and quartz windows of the QTA. The sensitivity of the chemical vapor-generating element determination is largely influenced by the surface condition of the quartz components of the QTA. Additionally, it is possible that sample droplets containing Si carried from the reaction cell into the QTA generate the SiO radical absorption band ($X^1\Sigma^+ \rightarrow A^1\Pi$, $E_{ex} = 5.31$ eV, 216.03 nm (1, 6), 217.66 nm (0, 4), 219.74 nm (1, 5), 250.99 nm (3, 1), 256.38 nm (3, 0)), which could cause spectral interferences with the Te, Sb, Bi, and Hg lines. However, such interferences were not evaluated in this study, as hydrofluoric acid was not used.[21]

For the pre-reduction of As(v) and Sb(v), aliquot volumes of up to 40 mL of the digest were mixed in 50 mL flasks with 2.5 mL of 37% (m/m) HCl and 5 mL of 0.5 mol $L^{-1}$ thiourea solution, heated on a water bath at 90 °C for 30 minutes, cooled and made up to the mark, similar to the procedures previously reported.[10,24] The concentrations in the final solution, from which the As and Sb were determined, were 0.5 mol $L^{-1}$ HCl and 0.05 mol $L^{-1}$ thiourea. In the case of Bi and Hg, only 2.5 mL HCl 37% solution was added so that the final concentration of HCl in the analyzed samples was 0.5 mol $L^{-1}$. Thiourea was not added in the case of these elements, as the pre-reduction was not necessary. For the pre-reduction of Se(vi) and Te(vi), a heat-assisted pre-reduction with HCl was applied. 29 mL of 37% (m/m) HCl solution was added to aliquot volumes of up to 10 mL from the digest and heated in a water bath at 90 °C for 30 min. Then, a supplementary treatment of the sample in 7 mol $L^{-1}$ HCl was applied to overcome the nitrite and $NO_x$ interferences on Se and Te determination.

### Method validation

The CVG-HR-CS QTAAS method was validated through analytical performances, such as instrumental LODs, method LODs in real samples, accuracy (recovery and precision), and linearity of the calibration curves using the WIA procedure for the absorbance signals. The number of pixels of the WIA signal was established in order to ensure the linearity of the calibration curves and good sensitivity of the method. The instrumental LODs were evaluated based on the $3\sigma$ criterium (LOD = $3s_b/m$, where $s_b$ is the deviation standard of the blank sample signal for $n = 11$ measurements in the WIA procedure, and $m$ is the slope of the calibration curve). The limits of detection of the method expressed as mg $kg^{-1}$ in real samples were evaluated based on the instrumental values and sample preparation protocol. The accuracy of the method was evaluated by analyzing several CRMs through recovery and extended uncertainty in the laboratory for $n = 3$ parallel measurements and 95% confidence level, by which the presence of systematic errors was checked. In the case of samples where the analyte concentration was below the LOD values, recovery and expanded uncertainty were evaluated in spiked samples at a concentration of 5 μg $L^{-1}$ analyte. Evaluation of the performance of the CVG-HR-CS QTAAS method for CRMs and spiked samples was done by assessing the deviation of laboratory results from the assigned values based on the ($z'$ or $z$) score, in accordance with the Eurachem

Guide for analytical chemistry in Europe.[42] A score of $|z'$ or $z| \leq 2.0$ indicates satisfactory performance and generates no signal, while values between 2 and 3 indicate questionable performance and scores higher than 3 indicate unsatisfactory performance of the method. The contributions of the individual uncertainties of the representative steps in the analytical procedure (calibration of the standard sample and test sample preparation, calibration curve fitting and aliquots analysis) over the combined uncertainty allowed highlighting the steps with the most weight. The precision of the method, expressed as relative standard deviation (RSD%), was evaluated based on the laboratory combined uncertainty ($u_{c\text{-lab}}$).

## Results and discussion

### Optimization of the pre-reduction and CVG conditions for As, Sb, Hg, Bi, Se and Te determination by CVG-HR-CS QTAAS

The CVG-HR-CS QTAAS method was optimized in terms of the HCl and thiourea concentrations in the samples, $NaBH_4$ and NaOH concentrations and the volume of $NaBH_4$ added to a 5 mL aliquot volume of the sample in HCl medium, respectively. The hydrochloric acid concentration in the sample in the pre-reduction step was identical to that used in the CVG. The optimization was conducted on synthetic solutions in which $HNO_3$ was not added. The results, presented in ESI (Section 1, Fig. S1–S5),† indicate an optimal HCl concentration in the analyzed samples of 0.5 mol $L^{-1}$ in the presence of 0.05 mol $L^{-1}$ thiourea for the As and Sb determination, 0.5 mol $L^{-1}$ HCl for the Bi and Hg determination without thiourea and 7 mol $L^{-1}$ HCl without thiourea for Se and Te, respectively. The signal decreased significantly for Se and Te in the presence of 0.05 mol $L^{-1}$ thiourea; it is well known that the pre-reduction reagents used for As(v) and Sb(v) are too powerful for Se(vi) and Te(vi). In terms of Bi and Hg determination, the pre-reduction step is not necessary; therefore, the determination could be made directly from the digest in the presence of 0.5 mol $L^{-1}$ HCl without thiourea. Also, in the case of Bi and Hg determination from the solution in which As(v) and Sb(v) were pre-reduced, it was observed that in the presence of 0.05 mol $L^{-1}$ thiourea, the Hg signal decreased by approximately 10%, while the Bi signal was not significantly influenced. However, in the case of As, but especially in the case of Sb, the concentration of thiourea used for the pre-reduction was a critical parameter in the presence of 0.5 mol $L^{-1}$ HCl. This influence was also observed in higher HCl concentrations (1 mol $L^{-1}$ and 7 mol $L^{-1}$). However, by increasing the HCl concentration in the sample, the absorbance signals decreased significantly for As, Sb, Bi and Hg. Consequently, the selected optimum HCl concentration for As, Sb, Bi and Hg was 0.5 mol $L^{-1}$, while 0.05 mol $L^{-1}$ thiourea is necessary for the pre-reduction of As(v) and Sb(v), respectively. In terms of Se and Te determination, the depressive effect of thiourea on the absorbance signal was obvious, with the Se and Te signals decreasing approximately by 4 and 6 times, respectively, in the presence of 0.01 mol $L^{-1}$ thiourea. At concentrations higher than 0.03 mol $L^{-1}$ thiourea, the signal was almost completely suppressed. The depressive effect of thiourea became very severe at HCl concentrations lower than 7 mol $L^{-1}$ (*e.g.*, 0.5 and 1 mol $L^{-1}$). Therefore, a separate determination of Se and Te in 7 mol $L^{-1}$ HCl was selected without thiourea. The optimum concentrations for $NaBH_4$ and NaOH were 2.5% (m/v) and 0.1% (m/v), respectively, for a reagent volume of 2 mL for the As, Bi and Sb determination and 3.5 mL for Hg, Se and Te, at a 5 mL aliquot sample containing HCl at optimum concentration. The unified optimum working conditions are presented in Table 1.

### Elimination of nitrite, $NO_x$ and $O_2$ interferences for Se, Te, As, Sb and Bi determination by CVG-HR-CS QTAAS

Three procedures were investigated to overcome the nitrite and $NO_x$ interferences on Se and Te determination in the presence

Table 1 Optimum working conditions for the determination of As, Sb, Hg, Bi, Se and Te by CVG-HR-CS QTAAS

| | Setting | | |
|---|---|---|---|
| Parameter | Hg | As, Bi, Sb | Se, Te |
| Analytical wavelength (nm) | 253.652 Hg | 193.696 As<br>223.061 Bi<br>217.582 Sb | 196.027 Se<br>214.281 Te |
| Transient signal measurement | Peak height | Peak height | Peak height |
| Number of pixels associated with the WIA signal | 5 (CP ± 2) | 5 (CP ± 2) | 5 (CP ± 2) |
| QTA temperature (°C) | 150 ± 10 | 950 ± 10 | 950 ± 10 |
| Ar flow rate (L $h^{-1}$) | 6 | 6 | 6 |
| Spectrum recording time (s) | 10 | 10 | 10 |
| Pre-wash time of the reaction cell and QTA with Ar before $NaBH_4$ solution addition (s) | 0 | 20 As<br>20 Bi<br>30 Sb | 20 Se<br>20 Te |
| Purging time with Ar of the reaction cell after $NaBH_4$ addition (s) | 25 | 25 | 25 |
| Aliquot sample volume (mL) | 5 | 5 | 5 |
| HCl concentration in aliquot sample (mol $L^{-1}$) | 0.5 | 0.5 | 7 |
| Thiourea concentration in aliquot sample (mol $L^{-1}$) | — | 0.05 | — |
| Volume of $NaBH_4$ solution (mL) | 3.5 | 2 | 3.5 |
| $NaBH_4$ concentration (%, m/v) | 2.5 | 2.5 | 2.5 |
| NaOH concentration (%, m/v) | 0.1 | 0.1 | 0.1 |

 

of 10% (v/v) $HNO_3$ in synthetic samples with a concentration of 10 μg $L^{-1}$ Se(VI) and Te(VI), as follows: (i) decomposition of nitrite with sulfamic acid after the pre-reduction of Se(VI) and Te(VI) with concentrated HCl according to the procedure previously used by Lopes *et al.*;[33] (ii) decomposition of nitrite anions by sulfamic acid addition and nitrogen purging; and (iii) a simple purging of the sample with nitrogen. Therefore, in the first procedure, a volume of 5 mL sulfamic acid 10% (m/v) solution was added after the pre-reduction step of Se(VI) and Te(VI) by heating in a water bath in 7 mol $L^{-1}$ HCl. The yellow-brown color due to the presence of nitrite/nitrogen oxides disappeared. The solution was finally made up to 50 mL with HCl solution, resulting in a final concentration of 7 mol $L^{-1}$ HCl and 1% (m/v) sulfamic acid, from which the Se and Te signals were measured. In the second procedure, the previously obtained solution was subjected to a supplementary purge with nitrogen for a period of 10–30 min at room temperature. In the third procedure, a simple purging with nitrogen for 10–30 min after pre-reduction was applied without sulfamic acid addition. After the performance evaluation of the three procedures, these were applied for Se and Te determination in the CRM and real test samples by external calibration using standard solutions in 7 mol $L^{-1}$ HCl without $HNO_3$ addition.

The variation of the absorbance signal (CP ± 2 pixels) for Se and Te in synthetic samples after nitrite decomposition with sulfamic acid with or without nitrogen purging for 10–30 min after the pre-reduction step is presented in Fig. 1. In all cases, the influence of the pre-washing time (0–60 s) of the reaction cell and QTA with 6 L $h^{-1}$ Ar before adding the $NaBH_4$ solution was studied. In the absence of Ar pre-washing, the $NaBH_4$ solution was added immediately after the introduction of the sample into the reaction cell, followed by the purging of hydrides for 25 s into the QTA at the same Ar flow rate. The recorded spectra and transition signal for Se and Te in different working conditions are presented in ESI (Section 2, Fig. S6–S9).† As shown in the recorded spectra, Se and Te determination by CVG-HR-CS QTAAS is compromised without additional sample processing after the pre-reduction step and without pre-washing the reaction cell and QTA with Ar. Determination of Se and Te could be possible by nitrite decomposition with 1% (m/v) sulfamic acid solution, without purging the sample with nitrogen, and with/without pre-washing the reaction cell and QTA with Ar (ESI, Section 2, Fig. S6a, b, S8a and b†). It was observed that the addition of sulfamic acid prior to the pre-reduction did not show the desired outcome in terms of overcoming the depressive non-spectral interferences on Se and Te. The results are in accordance with the literature data, which indicated that nitrite has a more intense depressive effect than nitrate.[30] Also, the absorption signal of Se and Te could be measured without interferences using $N_2$ purging of the solution for 20 min and with/without pre-washing the reaction cell and QTA with Ar for 20 s (ESI, Section 2, Fig. S7c, d, S9c and d†), without 1% (m/v) sulfamic acid addition. In any case, the reaction cell and QTA pre-washing with Ar for 20 s had a critical influence not only on the absorption signal, but especially on the background signal noise, as can be seen in the spectra presented in the ESI (ESI, Section 2, Fig. S6–S9b and d†). Fig. 1

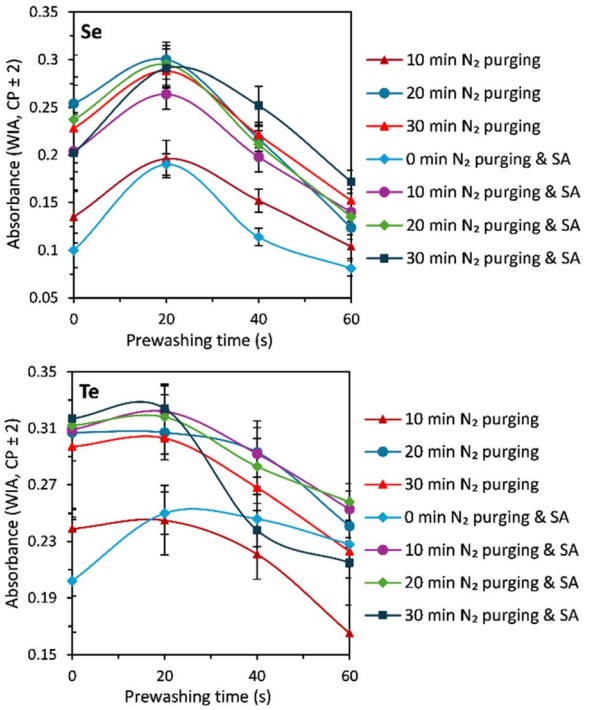


Fig. 1 Variance of the absorbance signal for Se (196.027 nm) and Te (214.281 nm) under various pretreatment conditions of the sample (7 mol $L^{-1}$ HCl and 10% (v/v) $HNO_3$), after the pre-reduction step and different pre-washing times of the reaction cell and QTA before the $NaBH_4$ addition.

shows a significant decrease of the absorption signal for Se and Te at the pre-washing times of 40 s and 60 s of the reaction cell and QTA, compared with that of 20 s, regardless of the pretreatment procedure of the sample, after the pre-reduction step. This behaviour could be explained by the fact that, indeed, the presence of oxygen traces in QTA, together with hydrogen, is beneficial for the atomization of Se and Te hydrides, similar to the results presented by Agterdenbos *et al.*[36] for Se determination and those of D'Ulivo and Dedina[37] for As and Se determination by the CVG QTAAS. The purging time with $N_2$ decreases from 20 to 10 min by the addition of 1% (m/v) sulfamic acid solution, with similar signals compared to the procedure that implies only $N_2$ purging of the sample for 20 min. In the procedure based on $N_2$ purging for 20 min without sulfamic acid addition, an improved sensitivity of 1.6 and 1.3 times was obtained for Se and Te, respectively, compared to the procedure based on sulfamic acid addition without $N_2$ purging. Nitrogen purging for 10 min after sulfamic acid addition led to an improvement of 1.4 and 1.3 times for Se and Te sensitivity, compared to the procedure based on sulfamic acid addition without $N_2$ purging. Therefore, based on the data presented in Fig. 1 and spectra in ESI (Section 2, Fig. S6–S9†), the optimal conditions for the elimination of nitrite and interferences caused by $NO_x$ and $O_2$ were: (i) $N_2$ purging of the samples for 20 min, after pre-reduction and 20 s Ar pre-washing of the reaction cell and QTA before adding the $NaBH_4$ solution; (ii) addition of 1% (m/v) sulfamic acid and $N_2$ purging for

10 min of the sample after pre-reduction, and 20 s Ar pre-washing of the reaction cell and QTA. Although the addition of sulfamic acid and pre-washing the reaction cell and QTA for 20 s would result in the elimination of spectral interferences, the sensitivity of the method was lower if a supplemental $N_2$ purging of the sample was not performed.

In the case of As, Sb and Bi determination, it was not necessary $N_2$ purging or sulfamic acid addition to the sample after pre-reduction. However, pre-washing the reaction cell and the QTA with Ar at 6 L $min^{-1}$ proved to be mandatory for 20 s (As and Bi) and 30 s (Sb) for the elimination of residual $NO_x$ that causes severe interferences on the As, Sb and Bi spectra. This pre-washing also ensures the removal of oxygen from the solution, which has the same severe interference on the CVG determination of elements by QTAAS at a ratio of $O_2/H_2 > 0.1$ due to the fine-structured absorption spectrum of $O_2$ below 200 nm. Pre-washing the reaction cell and QTA was not necessary in the case of Hg determination. The absorption spectra for As, Sb, Bi and Hg, recorded in these conditions and 10% (v/v) $HNO_3$ are presented in the ESI (Section 3, Fig. S10–S13).†

## Calibration curves and LODs

The variance of the WIA signal against the pixel number in the optimal conditions for the 3 procedures used for the elimination of nitrite and $NO_x$ interferences in the Se and Te determination by the CVG-HR-CS QTAAS are presented in ESI (Section 4, Fig. S14†), while those for As, Sb and Bi with the reaction cell and QTA pre-washing, and Hg without Ar pre-washing in ESI (Section 4, Fig. S15).† The profile of the As, Sb, Bi, Se and Te spectral lines was integrated on 7 pixels, while that of Hg was on 9 pixels. According to Fig. S14 and S15,† an insignificant increase of the WIA signal integrated over 7 and 9 pixels was observed, compared to the signal integrated on 5 pixels. Therefore, the sensitivity of the CVG-HR-CS QTAAS method, obtained by signal integration over CP ± 2, was 3.1–3.6 times higher for Se and 3.3–3.5 times higher for Te, compared to the signal measured on the central pixel (CP) of the analytical line. Thus, the HR-CS AAS technology advantage is remarkable with regard to sensitivity improvement. Furthermore, no differences were found between the linearity of the calibration curves for WIA signals recorded using 1, 3 and 5 pixels. Therefore, the analytical performances of the CVG-HR-CS QTAAS method were evaluated based on the calibration curves registered for the WIA signal on the CP ± 2 pixels. The calibration curve parameters and instrumental LODs for the CVG-HR-CS QTAAS method, and those in real samples, under optimal operating conditions, and elimination of nitrite, $NO_x$ and $O_2$ interferences over the Se and Te signals in the procedure with 20 min $N_2$ purging of the sample after pre-reduction in 7 mol $L^{-1}$ HCl and 20 s pre-washing with Ar of the reaction cell and QTA are presented in Table 2, together with those obtained for As, Sb and Bi, after pre-washing the reaction cell and QTA, and Hg without pre-washing.

According to Table 2, the CVG-HR-CS QTAAS method ensured a good reproducibility of the calibration curves and LODs, RSD values being in the range of 2.9–18.6% and 5.3–19.4%, respectively, for 7 days. The greater RSD values for LODs could be explained by the fact that they reflect the standard deviation of the slopes of the calibration curves and that of the signal for the blank solution ($n = 11$) for 7 days. The determination coefficients of the calibration curves were in the range of 0.9957–0.9993. The instrumental LODs (μg $L^{-1}$) for the HR-CS QTAAS method were 0.063 (Hg), 0.033 (As), 0.030 (Bi), 0.016 (Sb), 0.167 (Se) and 0.060 (Te), while those in the solid samples (mg $kg^{-1}$) were 0.031 (Hg), 0.016 (As), 0.015 (Bi), 0.008 (Sb), 0.084 (Se) and 0.030 (Te). The LODs of the method in the solid samples were approximately 3, 12, 300 and 625 times better than the normal values (mg $kg^{-1}$) in soil, namely, 0.1 (Hg), 1 (Se) and 5 (As and Sb), in compliance with the Ministerial Order No. 756/1997.[43] In the case of Bi, the LOD method in soil was approximately 8.5 times better than the normal content in the upper continental crust (0.127 mg $kg^{-1}$).[44] Tellurium has a low abundance in the continental crust, with concentrations as low as 1–5 μg $kg^{-1}$ in natural soils, with few exceptions in areas under anthropogenic mining activity of non-ferrous metals.[45] Therefore, little to no literature data exists regarding the Te normal content, and thus, an evaluation of the CVG-HR-CS QTAAS method suitability for the analysis of samples

Table 2 Parameters of the calibration curves, instrumental and method LODs obtained by CVG-HR-CS QTAAS over 7 days using absorbance measured at peak height of the transient signal and WIA procedure (CP ± 2) under optimum working conditions

| | Calibration curve parameters | | | | LOD | | LOQ[c] | |
|---|---|---|---|---|---|---|---|---|
| Element | Intercept | Slope (L $\mu g^{-1}$) | $R^2$ | Standard deviation of the blank ($s_b$) | Instrumental[a] (μg $L^{-1}$) | Method[b] (mg $kg^{-1}$) | Instrumental (μg $L^{-1}$) | Method (mg $kg^{-1}$) |
| Hg[d] | 0.0036 ± 0.0009 | 0.0196 ± 0.0012 | 0.9993 ± 0.0006 | 0.00041 | 0.063 ± 0.010 | 0.031 ± 0.005 | 0.210 ± 0.033 | 0.103 ± 0.017 |
| As[e] | 0.0450 ± 0.0085 | 0.0209 ± 0.0005 | 0.9968 ± 0.0085 | 0.00023 | 0.033 ± 0.005 | 0.016 ± 0.003 | 0.110 ± 0.017 | 0.053 ± 0.010 |
| Bi[e] | 0.0005 ± 0.0004 | 0.0573 ± 0.0049 | 0.9957 ± 0.0130 | 0.00057 | 0.030 ± 0.005 | 0.015 ± 0.002 | 0.099 ± 0.016 | 0.050 ± 0.007 |
| Sb[f] | 0.0081 ± 0.0008 | 0.0470 ± 0.0073 | 0.9979 ± 0.0036 | 0.00025 | 0.016 ± 0.002 | 0.008 ± 0.002 | 0.053 ± 0.007 | 0.027 ± 0.007 |
| Se[g] | 0.0074 ± 0.0026 | 0.0298 ± 0.0007 | 0.9968 ± 0.0060 | 0.00166 | 0.167 ± 0.008 | 0.084 ± 0.004 | 0.556 ± 0.027 | 0.279 ± 0.015 |
| Te[g] | 0.0042 ± 0.0006 | 0.0307 ± 0.0023 | 0.9970 ± 0.0061 | 0.00061 | 0.060 ± 0.010 | 0.030 ± 0.005 | 0.200 ± 0.034 | 0.100 ± 0.018 |

[a] Instrumental LOD calculated using the $3\sigma$ criterion (LOD = $3s_b/m$), where $s_b$ is the standard deviation of the blank signal ($n = 11$) and $m$ is the slope of the calibration curve. [b] LOD of the method calculated for 0.5 g digested sample, made up to 50 mL and 5 times dilution for the measurement. [c] LOQ – limit of quantification considered as 3.33 × LOD. [d] Hg – measured without pre-washing with Ar of the reaction cell and QTA. [e] As, Bi – measured with 20 s pre-washing of the reaction cell and QTA. [f] Sb – measured with 30 s pre-washing of the reaction cell and QTA. [g] Se, Te – measured with 20 min $N_2$ purging of the sample after pre-reduction and 20 s pre-washing of the reaction cell and QTA.

 

Table 3 Found values for Hg, As and Sb in food and environmental CRMs obtained by the sequential CVG-HR-CS QTAAS method

| CRM | Hg[a] | | As[a] | | Sb[a] | |
|---|---|---|---|---|---|---|
| | Certified value ± $U_{CRM}$[b] (mg kg$^{-1}$) | Found value ± $U_{lab}$ (mg kg$^{-1}$) | Certified value ± $U_{CRM}$[c] (mg kg$^{-1}$)[b] | Found value ± $U_{lab}$[c] (mg kg$^{-1}$) | Certified value ± $U_{CRM}$[b] (mg kg$^{-1}$) | Found value ± $U_{lab}$[c] (mg kg$^{-1}$) |
| Dried mushroom powder CS-M-3 | 2.849 ± 0.104 | 2.939 ± 0.359 | 0.651 ± 0.026 | 0.604 ± 0.105 | — | — |
| Fish muscle ERM-BB422 | 0.601 ± 0.030 | 0.574 ± 0.060 | 12.7 ± 0.7 | 12.0 ± 1.3 | — | — |
| Lobster hepatopancreas Tort-2 | 0.27 ± 0.06 | 0.25 ± 0.07 | 21.6 ± 1.8 | 21.0 ± 2.9 | — | — |
| Lobster hepatopancreas Tort-3 | 0.292 ± 0.022 | 0.305 ± 0.042 | 59.5 ± 3.8 | 62.0 ± 6.9 | — | — |
| Mussel tissue ERM-CE278k | 0.071 ± 0.007 | 0.076 ± 0.025 | 6.7 ± 0.4 | 7.0 ± 1.2 | — | — |
| Mussel tissue SRM 2976 | 61.0 ± 3.6 | 64.9 ± 7.6 | 13.3 ± 1.8 | 12.8 ± 3.1 | — | — |
| Tuna fish ERM-CE464 | 5.24 ± 0.10 | 4.95 ± 0.74 | — | — | — | — |
| Chicken GBW10018 | 0.0036 ± 0.0015 | <0.031 (LOD) | 0.109 ± 0.013 | 0.121 ± 0.037 | — | — |
| Bovine liver BCR-185R | — | — | 0.0330 ± 0.0029 | <0.053 (LOQ) | | |
| Lake sediment BCR-280R | 1.46 ± 0.20 | 1.39 ± 0.32 | 33.4 ± 2.9 | 32.4 ± 3.9 | — | — |
| Metals on soil CRM025-050 | 99.8 ± 18.0 | 94.0 ± 22.1 | 339 ± 20.5 | 319 ± 40.0 | <3.2 | 3.2 ± 0.4 |
| Sand CRM048-50 G | 28.0 ± 1.13 | 29.0 ± 5.97 | 123 ± 3.40 | 126 ± 23.88 | 139 ± 13.9 | 151 ± 25.2 |
| Soil LGC6141 | 1.2 | 1.0 ± 0.16 | 13.2 ± 3.5 | 12.3 ± 3.4 | — | — |
| Light sandy soil Metranal-32 | 0.120 | 0.134 ± 0.02 | 26.1 ± 1.1 | 27.9 ± 4.8 | — | — |
| Loam Metranal-34 | 0.21 | 0.21 ± 0.04 | 42.4 ± 2.2 | 44.8 ± 5.3 | — | — |
| River sediments NCS DC78301 | 0.22 ± 0.04 | 0.24 ± 0.05 | 56 ± 10 | 59 ± 12 | — | — |
| Loamy clay SQ001-30 G | 2.86 ± 0.1 | 2.77 ± 0.4 | 43.1 ± 0.7 | 44.6 ± 4.0 | 42.0 ± 4.1 | 39.0 ± 8.0 |
| Estuarine sediment ERM-CC580 | 132 ± 3 | 137 ± 16 | — | — | — | — |
| Pooled recovery (%) | — | 100 ± 17 | — | 101 ± 18 | — | 100 ± 17 |
| Precision (%) | — | 5.2–16.4 | — | 4.5–15.3 | — | 6.3–10.3 |
| $\|z'\|$ score[d] | — | 0.3–1.1 | — | 0.2–1.1 | — | 0.8–1.1 |

[a] Hg determined by external calibration without pre-washing the reaction cell and QTA; As and Sb determined by external calibration with 20 s and 30 s pre-washing the reaction cell and QTA, respectively. [b] $U_{CRM}$ – is the extended uncertainty from the certificate ($k = 2$, 95% confidence level). [c] $U_{lab}$ – is the extended uncertainty in the laboratory ($k = 2$, 95% confidence level, $n = 3$ repeated measurements). [d] $|z'|$ score calculated according to Eurachem guide.[42]

collected from the upper continental crust could not be performed. The instrumental LOD for Hg determination was 30 times better than the maximum allowed concentration in foods of marine origin of 1 mg kg$^{-1}$, according to decision 2023/915.[46] In the case of As, the LOD of the method was 6 and 25 times better than the maximum admitted levels for the total and inorganic As fraction (0.1–0.5 mg kg$^{-1}$) in different foods.[46] The LODs obtained by the CVG-HR-CS QTAAS method for Se and Te in the procedure based on 1% (m/v) sulfamic acid addition and 10 min $N_2$ purging of the sample were not significantly different than those obtained in the procedure based on a simple $N_2$ purging for 20 min, but they were much better than those obtained by the procedure using only sulfamic acid addition without $N_2$ purging and pre-washing the reaction cell and QTA. The LODs obtained by our CVG-HR-CS QTAAS method, compared to other sequential or simultaneous spectral multielemental methods, are presented in ESI (Section 5, Table S1).† The instrumental LODs obtained by the CVG-HR-CS QTAAS method were better than those obtained by the CVG-ICP-OES in our laboratory using the Spectro CIROS$^{CCD}$ spectrometer equipped with an HGX 200 CVG, Cetac (Nebraska, USA) for Hg (0.092 μg L$^{-1}$; 194.224 nm), Bi (0.300 μg L$^{-1}$; 190.241 nm), Sb (0.032 μg L$^{-1}$; 206.833 nm), Te (0.200 μg L$^{-1}$; 214.281 nm), but similar for As (0.031 μg L$^{-1}$; 189.042 nm), and poorer for Se (0.140 μg L$^{-1}$; 196.090 nm). The CVG-HR-CS QTAAS method presents better LODs for Hg and As compared to the FI-HR-CS-HG-QTAAS,[33] CVG-HR-CS ETAAS,[24,47] hydride generation slotted quartz tube atomizer high-resolution continuum source flame atomic absorption spectrometry (HG-STAT-HR-CS-FAAS)[48] and HG-ICP-OES,[10,49] but poorer compared to HG-ICP-MS method.[12,50,51] In the case of Bi, our LODs obtained by the CVG-HR-CS QTAAS were better compared to other methods based on atomic absorption, such as hydride generation (multi)atomizer QTAAS (HG-(MM)QTAAS),[52] hydride generation dielectric barrier discharge atomic absorption spectrometry (HG-DBD-AAS),[52] hydride generation flowing liquid anode atmospheric pressure discharge optical emission spectrometry,[53] and HG-ICP-OES, either obtained in our laboratory or that reported by Welna *et al.*[10] For Se and Te, the LODs were similar, or even better compared to the methods based on AAS,[48,52,54] but poorer than those reported by AFS[8,55] and HG-ICP-OES/MS.[10,12,49,50] Even though the LODs obtained for Sb were better than those reported by HG-ICP-OES,[10,49] unfortunately, they were poorer than those obtained by the ETAAS method coupled with diverse preconcentration procedures[24,47] and HG-ICP-MS without preconcentration.[50,51]

## Accuracy of the CVG-HR-CS QTAAS method

The recoveries of Hg, As and Sb in several food items, water sediments and soil CRMs, obtained by the CVG-HR-CS QTAAS, are presented in Table 3. The recovery for Se determination in

the CRM samples, using different procedures for the sample treatment in order to eliminate nitrite, $NO_x$ and $O_2$ interferences, are presented in Table 4. Based on the recovery in food and environmental CRM samples (Table 3) of 100% ± 17% (Hg), 101% ± 18% (As) and 100% ± 17% (Sb) it can be concluded that the CVG-HR-CS QTAAS method is not affected by systematic errors in such samples, as the expanded uncertainty for the pooled recovery includes the 100% value ($k = 2$, 95% confidence level, $n = 3$). The $|z'|$ score values in the range 0.2–1.1 ≤ 2 indicate satisfactory performance for the CVG-HR-CS QTAAS method and generate no signal. In the case of Se determination in the food and environmental CRM samples, the CVG-HR-CS QTAAS method is prone to significant negative bias (recovery 63% ± 23%, $k = 2$, 95% confidence level) when no treatment for eliminating nitrite, $NO_x$ and $O_2$ interferences was applied. Under this condition, the majority of the $|z'|$ values were higher than 3.0, indicating unsatisfactory performance and generating an action signal. In some samples (Chicken GBW10018 and Sand CRM048-50G), the $|z'|$ values were <2. However, the results are not reliable due to the poor repeatability of the measurements. Conversely, by purging the solutions with nitrogen for 20 min after pre-reduction in 7 mol $L^{-1}$ HCl or by the addition of 1% (m/v) sulfamic acid and $N_2$ purging for 10 min and 20 s prewashing with Ar of the reaction cell and QTA, the pooled recoveries of 101% ± 18% and 102% ± 18% were obtained, which demonstrate overcoming the depressive matrix effects in the CVG-HR-CS QTAAS method using any of the two sample treatment procedures. Satisfactory performance was also highlighted by the $|z'|$ values (0.1–1.2). The pooled recoveries and $|z'|$ scores for As, Sb and Se (for Se, the samples were purged with nitrogen for 20 min) in SRM® 3280 Multivitamin/Multielement Tablets also demonstrate the lack of systematic errors and satisfactory performance for all 3 elements (Table 5). The sample processing by $N_2$ purging for 20 min was also verified for the commercially available dietary supplements, obtaining a pooled recovery of 102% ± 11% and $|z|$ scores of 0.3–1.9 ≤ 2 (Table 6). In these samples, the concentrations of As, Sb, Bi and Te were below the LODs of the CVG-HR-CS QTAAS method; therefore, the results are not presented in the table.

For the food and environmental CRM samples, in which the concentration of elements was below the LOD, the accuracy of the method was verified in spiked samples with 5 μg $L^{-1}$ of the element. The recoveries and $|z'|$ scores presented in ESI (Section 6, Table S2†) also demonstrate that additional sample treatment by $N_2$ purging with or without sulfamic acid addition in the case of Te determination ensured good pooled recoveries and satisfactory performance of the method ($|z'|$ scores 0–1.6 ≤ 2). A significant negative systematic error could be observed in the samples without any pretreatment methods for overcoming the nitrite, $NO_x$ and $O_2$ interferences (recovery 30% ± 22%; $|z'|$ scores 6.7–25.3 > 3). Satisfactory results were obtained in all spiked samples in the case of Sb, while in the case of Bi, in 14 samples out of 16. In two samples of fish muscle and lobster hepatopancreas, the spiked values for Bi presented negative systematic errors and questionable performance (2.0 < $|z = 2.6|$ < 3.0). The composition of the multielemental matrix obtained by ICP-OES in the analyzed CRM samples, which does not cause matrix effects for As, Hg and Sb determination, and Se and Te by CVG-HR-CS QTAAS, is presented in ESI (Section 7, Table S3).†

Table 4 Results for Se determination in CRMs by CVG-HR-CS QTAAS with and without various sample treatments and external calibration

| | | Found value ± $U_{lab}$[b] (mg $kg^{-1}$) | | |
|---|---|---|---|---|
| CRM | Certified value ± $U_{CRM}$[a] (mg $kg^{-1}$) | Without treatment[c] | $N_2$ purging[d] | $N_2$ purging and sulfamic acid addition[e] |
| Bovine liver BCR-185R | 1.68 ± 0.14 | 2.89 ± 0.75 | 1.60 ± 0.28 | 1.62 ± 0.300 |
| Dried mushroom powder CS-M-3 | 17.43 ± 1.36 | 1.72 ± 0.18 | 16.93 ± 2.83 | 18.73 ± 2.75 |
| Pig kidney ERM-BB186 | 10.3 ± 0.9 | 4.4 ± 1.0 | 10.9 ± 1.8 | 11.1 ± 1.5 |
| Fish muscle ERM-BB422 | 1.33 ± 0.13 | 0.80 ± 0.18 | 1.42 ± 0.28 | 1.27 ± 0.20 |
| Mussel tissue ERM-CE278k | 1.62 ± 0.12 | 0.74 ± 0.18 | 1.72 ± 0.33 | 1.74 ± 0.26 |
| Mussel tissue SRM 2976 | 1.80 ± 0.15 | 0.80 ± 0.12 | 1.69 ± 0.22 | 1.81 ± 0.31 |
| Lobster hepatopancreas Tort-2 | 5.63 ± 0.67 | 0.44 ± 0.11 | 5.97 ± 0.86 | 5.67 ± 1.20 |
| Lobster hepatopancreas Tort-3 | 10.9 ± 1.0 | 1.1 ± 0.2 | 10.8 ± 1.8 | 10.7 ± 1.8 |
| Chicken GBW10018 | 0.49 ± 0.06 | 0.45 ± 0.10 | 0.48 ± 0.12 | 0.48 ± 0.09 |
| Lake sediment BCR-280R | 0.46 ± 0.09 | 0.61 ± 0.17 | 0.43 ± 0.10 | 0.48 ± 0.11 |
| Metals on soil CRM025-050 | 518 ± 31 | 57 ± 13 | 533 ± 68 | 524 ± 68 |
| Sand CRM048-50 G | 178 ± 5.68 | 180 ± 35.78 | 186 ± 21.12 | 188 ± 31.18 |
| Soil LGC6141 | 0.5 | 0.5 ± 0.1 | 0.5 ± 0.1 | 0.5 ± 0.1 |
| River sediment NCS DC78301 | 0.39 ± 0.10 | 0.21 ± 0.07 | 0.41 ± 0.12 | 0.40 ± 0.11 |
| Loamy clay SQ001-30G | 154 ± 3 | 94 ± 17 | 151 ± 18 | 159 ± 15 |
| Pooled recovery (%) | — | 63 ± 23 | 101 ± 18 | 102 ± 18 |
| Precision (%) | — | 5.2–16.7 | 5.7–14.6 | 4.7–13.8 |
| $|z'|$ score[f] | — | 0.1–27.6 | 0.1–1.0 | 0.1–1.2 |

[a] $U_{CRM}$ – is the extended uncertainty from the certificate ($k = 2$, 95% confidence level). [b] $U_{lab}$ – is the extended uncertainty in the laboratory ($k = 2$, 95% confidence level, $n = 3$ repeated measurements). [c] Without $N_2$ purging and 1% (m/v) sulfamic acid addition after the pre-reduction and 20 s Ar pre-washing of the reaction cell and QTA. [d] $N_2$ purging of the samples for 20 min after pre-reduction and 20 s Ar pre-washing of the reaction cell and QTA. [e] 1% (m/v) sulfamic acid addition and $N_2$ purging for 10 min of the sample after pre-reduction and 20 s Ar pre-washing of the reaction cell and QTA. [f] $|z'|$ score calculated according to Eurachem guide.[42]

 

Table 5 Results obtained for As, Sb and Se concentrations in the SRM® 3280 multivitamin/multielement tablets by CVG-HR-CS QTAAS using external calibration

| Element | Certified value ± $U_{CRM}$[a] (mg kg$^{-1}$) | Found value ± $U_{lab}$[b] (mg kg$^{-1}$) | Recovery ± $U_{lab}$[b] (%) |
|---|---|---|---|
| As | 0.132 ± 0.044 | 0.133 ± 0.047 | 101 ± 35 |
| Sb | 0.159 ± 0.008 | 0.160 ± 0.026 | 101 ± 16 |
| Se[c] | 17.42 ± 0.45 | 17.96 ± 2.09 | 103 ± 12 |
| $\|z'\|$ score[d] | — | 0.1–0.5 | — |

[a] $U_{CRM}$ – is the extended uncertainty from the certificate ($k = 2$, 95% confidence level). [b] $U_{lab}$ – is the extended uncertainty in the laboratory ($k = 2$, 95% confidence level, $n = 3$ repeated measurements). [c] $N_2$ purging of the samples for 20 min after pre-reduction and 20 s Ar pre-washing of the reaction cell and QTA. [d] $|z'|$ score calculated according to Eurachem guide.[42]

Table 6 Results obtained for Se determination in dietary supplements by the CVG-HR-CS QTAAS method using external calibration[a]

| Name | Declared value (μg per capsule) | Found value ± $U_{lab}$[b] (μg per capsule) | Recovery ± $U_{lab}$[b] (%) | RSD (%) |
|---|---|---|---|---|
| Sup 1 | 32.14 | 32.46 ± 2.62 | 101 ± 8 | 4.0 |
| Sup 2 | 76.92 | 72.84 ± 8.76 | 95 ± 12 | 6.0 |
| Sup 3 | 166.67 | 176.74 ± 18.01 | 106 ± 10 | 5.1 |
| Sup 4 | 6.67 | 6.93 ± 1.19 | 104 ± 17 | 8.6 |
| Sup 5 | 11.76 | 12.60 ± 1.04 | 107 ± 8 | 4.1 |
| Sup 6 | 116.50 | 118.11 ± 11.55 | 101 ± 11 | 4.9 |
| Pooled recovery ± $U_{lab}$[b] (%) | | — | 102 ± 11 | — |
| $\|z\|$ score[c] | | 0.3–1.9 | — | — |

[a] $N_2$ purging of the samples for 20 min after pre-reduction and 20 s Ar pre-washing of the reaction cell and QTA. [b] $U_{lab}$ – is the extended uncertainty in the laboratory ($k = 2$, $n = 3$ repeated measurements and 95% confidence level). [c] $|z|$ score calculated according to Eurachem guide.[42]

## Precision of the CVG-HR-CS QTAAS method

The results for Hg, As, Sb, Bi, Se and Te by the CVG-HR-CS QTAAS method in the environmental test samples, namely the sludge from water treatment plants, water sediments and soil, are presented in Table 7. The precision based on extended uncertainties ($k = 2$, 95% confidence level, $n = 3$ repeated measurements) was in the range of 4.6–10.7%. Unfortunately, in many samples, the concentrations were below the LODs of the CVG-HR-CS QTAAS method. In these samples, the precision was checked by spiking the samples with 5 μg L$^{-1}$ element, obtaining the RSD values between 4.4% and 10.5% (ESI, Section 8, Table S4†). The pooled recoveries for the spiked concentration were in the range of 98–103% with an expanded uncertainty of ±(11–15)%, while the $|z|$ scores were in the range of 0.1–1.6, indicating a satisfactory performance of the method. For the Se determination in dietary supplements using nitrogen purging, the values for RSD% were between 4.0%–8.6% (Table 6).

In terms of the error sources, the highest weight had aliquot analysis (55–71%), followed by calibration fitting (9–27%) and

Table 7 Concentrations of As, Sb, Bi, Hg, Se and Te in real environmental test samples determined by the CVG-HR-CS QTAAS method using external calibration

| | Mean concentration ± $U_{lab}$[a] (mg kg$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| Sample | Hg[b] | As[b] | Sb[b] | Bi[b] | Se[c] | Te[c] |
| Sludge | <0.031[d] | <0.016[d] | <0.008[d] | 4.19 ± 0.45 | <0.084[d] | <0.030[d] |
| Sediment 1 | <0.031 | 9.86 ± 0.90 | <0.008 | 1.63 ± 0.31 | <0.084 | <0.030 |
| Sediment 2 | <0.031 | 7.36 ± 1.39 | <0.008 | <0.015[d] | <0.084 | <0.030 |
| Soil 1 | <0.031 | 2.81 ± 0.60 | <0.008 | <0.015 | <0.084 | <0.030 |
| Soil 2 | 4.23 ± 0.52 | 46.33 ± 4.43 | 2.15 ± 0.26 | 23.64 ± 2.28 | 3.21 ± 0.56 | <0.030 |
| Soil 3 | <0.031 | 26.02 ± 3.29 | <0.008 | 1.62 ± 0.28 | <0.084 | <0.030 |
| Soil 4 | 1.92 ± 0.38 | 9.25 ± 1.70 | <0.008 | 3.72 ± 0.40 | <0.084 | <0.030 |
| Soil 5 | <0.031 | 25.18 ± 2.82 | <0.008 | 31.68 ± 3.82 | <0.084 | <0.030 |
| Precision (%) | 6.1–9.9 | 4.6–10.7 | 4.8 | 4.8–9.5 | 8.7 | — |

[a] $U_{lab}$ – is the extended uncertainty in the laboratory ($k = 2$, 95% confidence level, $n = 3$ repeated measurements). [b] Hg was determined without pre-washing the reaction cell and QTA; As and Bi were determined with 20 s, and Sb with 30 s pre-washing the reaction cell and QTA. [c] Se and Te were determined by $N_2$ purging of the samples for 20 min after pre-reduction, and 20 s Ar pre-washing of the reaction cell and QTA. [d] Values represent the LOD of the CVG-HR-CS QTAAS method.

standards and sample preparation (18–21%). The composition of the multielemental matrix in real test samples is presented in ESI (Section 7, Table S3).†

## Conclusions

This study highlighted the analytical performance of the sequential multielemental CVG-HR-CS QTAAS method for determining several CVG elements (As, Sb, Bi, Hg, Se and Te) in various matrices after the microwave-assisted digestion in *aqua regia* and $HNO_3$ and $H_2O_2$ mixture and classical CVG using $NaBH_4$ solution in an HCl medium. The methods for overcoming non-spectral interferences from nitrite and $NO_x$ using various sample pretreatment procedures and $NO_x$ and $O_2$ spectral interferences by pre-washing the reaction cell and QTA with Ar were investigated. Mercury, As, Sb and Bi could be determined using the same CVG condition after the As(v) and Sb(v) pre-reduction with thiourea. Selenium and Te could be determined only separately from the other elements due to the different conditions for the pre-reduction, sample pretreatment procedures and CVG. Mercury was easier to determine compared to the other elements because its analytical line was not affected by spectral interferences from $NO_x$ and $O_2$, and any pretreatment of the sample and pre-washing the reaction cell and QTA was not necessary. The analytical results showed that critical attention should be paid to pre-washing the reaction cell and the QTA with Ar for a couple of seconds before the introduction of the $NaBH_4$ solution for As, Sb, Bi, Se and Te regardless of the sample pretreatment by sulfamic acid addition or $N_2$ purging. This step was necessary due to the elevated background signal and noise induced by the presence of $NO_x$ and $O_2$. The CVG-HR-CS QTAAS method proved to be highly efficient in eliminating these spectral interferences after a simple pre-washing of the reaction cell and QTA with Ar before adding the $NaBH_4$ solution. It was highlighted that a simple purging with nitrogen with or without sulfamic acid addition, after the pre-reduction step of (Se(vi) and Te(vi)) was the most suitable as it ensured the best sensitivity. It was observed that by sulfamic acid addition, the necessary time for nitrogen purging could be reduced, obtaining a similar sensitivity to that by simple nitrogen purging. The CVG-HR-CS QTAAS method proved to be sensitive, precise, accurate with a simple background correction and broadly applicable, with satisfactory performance, regardless of the matrix nature and multielemental composition, which allowed the use of external calibration. The developed method was characterized by LODs that were generally better or similar to other spectrometric techniques based either on direct liquid or solid sampling by HR-CS GFAAS, ICP-OES and ICP-MS with and without CVG.

## Data availability

The data supporting this article have been included within the article and ESI,† while those mentioned in the simple summary statement are available from the corresponding author upon reasonable request.

## Author contributions

Bettina Dora Szeredai: writing – original draft, methodology, investigation, formal analysis, data curation. Tiberiu Frentiu: supervision, funding acquisition, conceptualization. Norbert Muntean: methodology, investigation, formal analysis, data curation. Adrian-Ioan Dudu: writing – review & editing, validation. Eniko Covaci: writing – review & editing, visualization, software, resources, project management.

## Conflicts of interest

There are no conflicts of interest to declare.

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