



**BABEȘ-BOLYAI UNIVERSITY OF CLUJ-NAPOCA**  
**FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING**  
**DOCTORAL SCHOOL OF CHEMISTRY**

## **ABSTRACT OF PHD THESIS**

**Multielemental Methods for the Sequential Determination  
of Chemical Vapor-Generating Elements by  
High-Resolution Continuum Source Quartz Tube  
Atomic Absorption Spectrometry**

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**Cluj-Napoca  
2025**



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Spectrometry**

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## Contents

<b>KEYWORDS .....</b>	<b>6</b>
<b>LIST OF ABBREVIATIONS .....</b>	<b>7</b>
<b>INTRODUCTION .....</b>	<b>10</b>
Motivation of the Research Topic .....	10
Objectives and Research Methodology .....	11
<b>CHAPTER 1. HIGH-RESOLUTION CONTINUUM SOURCE ATOMIC ABSORPTION SPECTROMETRY VERSUS LINE SOURCE ATOMIC ABSORPTION SPECTROMETRY .....</b>	<b>12</b>
1.1. Short History of the Atomic Absorption Spectrometry .....	12
1.2. Appearance of the High-Resolution Continuum Source Atomic Absorption Spectrometry as Alternative to the Onewith Line Source .....	12
1.3. Comparison between the Low-Resolution Line Source Atomic Absorption Spectrometry (LR-LS AAS) and the High-Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS).....	13
1.4. Applications of the HR-CS AAS Analytical Technology .....	16
1.4.1. Applications of the HR-CS FAAS Analytical Technology.....	16
1.4.2. Applications of the HR-CS GFAAS Analytical Technology.....	17
1.4.3. Applications of the HR-CS QTAAS Analytical Technology .....	17
<b>CHAPTER 2. DETERMINATION OF AS, SB, BI, HG, SE AND TE IN FOOD AND ENVIRONMENTAL SAMPLES BY HIGH-RESOLUTION CONTINUUM SOURCE QUARTZ TUBE ATOMIC ABSORPTION SPECTROMETRY AND CHEMICAL VAPOR GENERATION .....</b>	<b>19</b>
2.1. Situation at International Level. Working Hypothesis and Research Objectives .....	19
2.2. Materials and Method.....	19
2.2.1. CVG-HR-CS QTAAS Instrumentation.....	19
2.2.2. Sample Preparation .....	21
2.3. Results and Discussion.....	22
2.3.1. Optimization of the Prereduction and CVG Conditions for the Determination of As, Sb, Hg, Bi, Se and Te with CVG-HR-CS QTAAS.....	22
2.3.2. Elimination of the Nitrite, NO <sub>x</sub> and O <sub>2</sub> Interferences for the Determination of Se, Te, As, Sb and Bi by CVG-HR-CS QTAAS .....	23
2.3.3. Calibration Curves and LODs in the CVG-HR-CS QTAAS Method.....	29

2.4. Accuracy of the CVG–HR–CS QTAAS Method.....	31
2.5. Precision of the CVG–HR–CS QTAAS Method .....	36
2.6. Conclusions.....	39
 <b>CHAPTER 3. THE METHOD WITH BROAD APPLICABILITY FOR THE COMPREHENSIVE EVALUATION OF SELECTED TOXIC ELEMENT CONTENT OF RECYCLABLE (BIO)PLASTICS BASED ON HIGH-RESOLUTION CONTINUUM SOURCE QUARTZ TUBE/FLAME ATOMIC ABSORPTION SPECTROMETRY .....</b>	
<b>41</b>	
3.1. Situation at International Level. Working Hypotheses and Research Objectives .....	41
3.2. Materials and Method.....	41
3.2.1. CVG–HR–CS QTAAS and HR–CS FAAS Instrumentation.....	41
3.2.2. Preparation and Analysis of Recyclable (Bio)plastic Material Samples.....	42
3.2.3. Validation of the CVG-HR-CS QTAAS and HR-CS FAAS Methods for the Analysis of Recyclable (Bio)plastic Materials .....	42
3.3. Results and Discussion.....	43
3.3.1. Optimum Working Conditions for the Determination of As, Sb, Bi and Hg by CVG-HR-CS QTAAS and Metals by HR-CS FAAS in (Bio)plastic Materials .....	43
3.3.2. Performance Study of the CVG-HR-CS QTAAS and HR-CS FAAS Methods for the Analysis of (Bio)plastic Materials .....	44
3.3.3. Accuracy and Precision of the CVG-HR-CS QTAAS and HR-CS FAAS Methods for the Analysis of (Bio)plastic Materials .....	46
3.3.4. Element Content According to the Origin and Type of the Recyclable (Bio)plastic Materials.....	48
3.4. Conclusions.....	55
 <b>CHAPTER 4. NOVELTY ELEMENTS AND ORIGINAL CONTRIBUTIONS OF THE PHD THESIS. GENERAL CONCLUSIONS .....</b>	
<b>57</b>	
<b>REFERENCES.....</b>	<b>60</b>
<b>ACKNOWLEDGEMENTS.....</b>	<b>64</b>
<b>LIST OF PUBLISHED ARTICLES IN ISI JOURNALS DURING THE PHD PROGRAM.....</b>	<b>65</b>
<b>LIST OF SCIENTIFIC COMMUNICATIONS WHERE RESULT OF THE PHD THESIS WERE DISSEMINATED .....</b>	<b>65</b>

## **Keywords**

High-resolution continuum source atomic absorption spectrometry

Chemical vapor-generating elements

Quartz tube atomic absorption

Analytical performance

Non-spectral interferences

Spectral interferences

Method validation

Toxic elements

Recyclable (bio)polymeric materials

Applications

## List of Abbreviations

Abbreviation	Description in Romanian language	Description in English language
2D	Integrare semnal-lungime de undă	Integration signal-wavelength
3D	Integrare semnal-lungime de undă-timp	Integration signal-wavelength-time
AAS	Spectrometrie de absorbție atomică	Atomic absorption spectrometry
ABS	Acrilonitril butadien stiren	Acrylonitrile butadiene styrene
AFS	Spectrometrie de fluorescență atomică	Atomic fluorescence spectrometry
CCD	Detector cu sarcină cuplată	Charge-coupled device
CP	Pixel central	Central pixel
CRM	Material certificat de referință	Certified reference material
CVG	Generare de vapori chimici	Chemical vapor generation
CVG–HR–CS ETAAS	Generare de vapori chimici și detecție prin spectrometria de absorbție atomică de înaltă rezoluție cu sursă continuă cu evaporare electrotermică	Chemical vapor generation high-resolution continuum source electrothermal atomic absorption spectrometry
CVG–HR–CS QTAAS	Generare de vapori chimici și detecție prin spectrometria de absorbție atomică de înaltă rezoluție cu sursă continuă în tub de cuarț	Chemical vapor generation high-resolution continuum source quartz tube atomic absorption spectrometry
CVG–ICP–OES	Generare de vapori chimici și detecție prin spectrometria de emisie optică în plasma cuplată inductiv	Chemical vapor generation inductively coupled plasma optical emission spectrometry
CS–AAS	Spectrometria de absorbție atomică cu sursă de spectru continuu	Continuum source atomic absorption spectrometry
DBD	Microplasma cu barieră de dielectric	Dielectric barrier discharge
DEMON	Monocromator dublu Echelle	Double Echelle monochromator
EDXRF	Spectrometria de fluorescență cu raze X cu dispersie după energie	Energy dispersive X-ray fluorescence spectrometry
FAAS	Spectrometrie de absorbție atomică în flacără	Flame atomic absorption spectrometry
GFAAS	Spectrometrie de absorbție atomică în cuptor de grafit	Graphite furnace atomic absorption spectrometry
HCL	Lampa cu catod cavitat	Hollow-cathode lamp
HG	Generare de hidrură	Hydride generation
HG–(MM)QTAAS	Generare de hidrură și detecție prin spectrometria de absorbție atomică cu multiatomizor în tub de cuarț	Hydride generation multiple microflame quartz tube atomizer tube atomic absorption spectrometry

HG/CV-HR-CS QTAAS	Generare de hidrură/vapori reci și detecție prin spectrometria de absorbție atomică în tub de cuarț de înaltă rezoluție cu sursă continuă	Hydride generation/cold vapour generation high-resolution continuum source quartz tube atomic absorption spectrometry
HG-AFS	Generare de hidrură și detecție prin spectrometria de fluorescență atomică	Hydride generation atomic fluorescence spectrometry
HG-HR-CS QTAAS	Generare de hidrură și detecție prin spectrometria de absorbție atomică în tub de cuarț de înaltă rezoluție cu sursă continuă	Hydride generation high-resolution continuum source quartz tube atomic absorption spectrometry
HG-HR-CS FAAS	Generare de hidrură și detecție prin spectrometria de absorbție atomică în flacără de înaltă rezoluție cu sursă continuă	Hydride generation high-resolution continuum source flame atomic absorption spectrometry
HG-ICP-MS	Generare de hidrură și detecție prin spectrometria de masă în plasma cuplată inductiv	Hydride generation inductively coupled plasma mass spectrometry
HG-ICP-OES	Generare de hidrură și detecție prin spectrometria de emisie optică în plasma cuplată inductiv	Hydride generation inductively coupled plasma optical emission spectrometry
HP-MAWD	Digestia umedă de înaltă presiune asistată de microunde	High-pressure microwave-assisted wet digestion
HR-CS AAS	Spectrometrie de absorbție atomică de înaltă rezoluție cu sursă continuă	High-resolution continuum source atomic absorption spectrometry
HR-CS FAAS	Spectrometrie de absorbție atomică în flacără de înaltă rezoluție cu sursă de spectru continuu	High-resolution continuum source flame atomic absorption spectrometry
HR-CS GFAAS	Spectrometrie de absorbție atomică în cuptor de grafit de înaltă rezoluție cu sursă continuă	High resolution continuum source graphite furnace atomic absorption spectrometry
ICP	Plasma cuplată inductiv	Inductively coupled plasma
ICP-MS	Spectrometrie de masă în plasma cuplată inductiv	Inductively coupled plasma mass spectrometry
ICP-OES	Spectrometrie de emisie optică în plasma cuplată inductiv	Inductively coupled plasma optical emission spectrometry
LA-ICP-OES/MS	Spectrometrie de emisie optică sau de masă în plasma cuplată inductiv cu ablație laser	Laser ablation inductively coupled plasma optical emission spectrometry or mass spectrometry
LOD	Limita de detecție	Limit of detection
LOQ	Limita de determinare	Limit of quantification
LR-LS FAAS	Spectrometrie de absorbție atomică în flacără de joasă rezoluție cu sursă de linii	Low-resolution line source flame atomic absorption spectrometry



LR-LS GFAAS	Spectrometrie de absorbție atomică în cuptor de grafit de joasă rezoluție cu sursă de linii	Low-resolution line source graphite furnace atomic absorption spectrometry
LS-AAS	Spectrometrie de absorbție atomică cu sursă de linii	Line source atomic absorption spectrometry
OPE	Polietilenă oxo-biodegradabilă	Oxo-biodegradable polyethylene
PA-PE/PA	Ambalaje din hârtie-polietilenă-poliamidă	Paper-polyethylene-polyamide
PC	Policarbonat	Polycarbonate
PE	Polietilenă	Polyethylene
PET	Tereftalat de polietilenă	Polyethylene terephthalate
PMT	Fotomultiplicator	Photomultiplier tube
PP	Polipropilenă	Polypropylene
PS	Polistiren	Polystyrene
PTFE	Politetrafluoroetilenă	Polytetrafluoroethylene
PVC	Policlorură de vinil	Polyvinyl chloride
QTA	Atomizor cu tub de cuarț	Quartz Tube Atomizer
RP-DLLME	Microextracție dispersivă lichid-lichid cu fază inversă	Reverse Phase Dispersive Liquid-Liquid Microextraction
RSD	Deviația standard relativă	Relative Standard Deviation
SPE	Extracție pe fază solidă	Solid-phase extraction
SPME	Microextracție pe fază solidă	Solid phase microextraction
Std. Dev.	Deviație standard	Standard deviation
UV-PVG	Generare fotoindusă de vapori chimici sub acțiunea radiațiilor UV	UV-photochemical vapor generation
WEEE	Deșeuri rezultate din echipamente electrice și electronice	Waste from electrical and electronic equipment
WIA	Absorbanța integrată în funcție de lungimea de undă	Wavelength-integrated absorbance
WSA	Absorbanța la o lungime de undă selectată	Wavelength-selected absorbance

## **Introduction**

### **Motivation of the Research Topic**

The development of the sample preparation procedures and the determination of the toxic and/or essential elements in rapid sequential or simultaneous regimen by spectrometric methods, which can ensure high sensitivity and selectivity, without spectral and non-spectral interferences by the concomitants' side from the original sample and/or resulted from the preparation reagents, continues to be of wide interest for the scientific community. Most data related to element content in various samples were obtained by line source atomic absorption spectrometry, which, unfortunately, has been put into a shadow 35 years ago, as a result of the impetuous development of the optical emission spectrometry and/or inductively coupled plasma mass spectrometry, much more efficient by the simultaneous character and high sensitivity. This was effective until 2003, when the Analytik Jena (Jena, Germany) company launched on the market the innovative instrumental technology based on high-resolution continuum source atomic absorption spectrometry (HR-CS AAS), on the basis of the instrumental concept proposed by the team of Becker-Ross at the Analytical Chemistry Institute of Berlin, Germany, as alternative to the low-resolution line source atomic absorption spectrometry (LR-LS AAS). The HR-CS AAS instrumental technology is in full development, despite the fact that there is only one manufacturer, Analytik Jena, on the market, as it managed to lift the competitiveness of the AAS method, by the elimination of the evident limitations of LR-LS AAS, by: (i) increasing the speed of the sequential analysis by the use of a single external source with continuous spectrum (Xe lamp) for the determination of all elements; (ii) simultaneous measurement and correction of the continuous background and fine structure of the molecular bands over the analytical lines in the spectral range below 250 nm; (iii) the increase of the sensitivity by the possibility of integration of the signal on the width of the spectral line, as a result of the use of the charged-couple device (CCD) as detector, in which each pixel generates a signal and it acts as a microdetector. A special class of elements which need to be determined in a sample it is formed by the chemical vapor-generating (CVG) elements, particularly composed of the elements of the main groups V and VI (As, Sb, Bi, Se, Te) together with Hg, whose determination is not an easy task, as a result of the differences between the necessary conditions of prereduction and derivatization, respectively the non-spectral interferences in liquid phase respectiv a interferențelor non-spectrale în faza lichidă on behalf of the nitrite anion and NO<sub>x</sub>, resulted from the reagents used during sample preparation, respectively the spectral interferences in the UV range because of the absorption bands on NO<sub>x</sub> and O<sub>2</sub>, purged in the liquid sample in the atomization cell. In the academic environment of Romania, the first HR-CS FAAS spectrometer equipped with two CVG derivatization systems and quartz tube as atomizer, was purchased by the Babeș-Bolyai University, on which the research of

the present PhD thesis was conducted, which being the first in Romania on this topic, represents an absolute novelty in the country.

## **Objectives and Research Methodology**

Based on the stage of the applicative development of the HR-CS AAS instrumental technology, under which was evidenced the motivation of the research topic, the main objective of the PhD thesis was the development and analytical characterization analitică of an analytical technology for the determination of chemical vapor-generating elements (As, Sb, Bi, Hg, Se and Te), in sequential regimen by high-rezolution continuum source quartz tube atomic absorption spectrometry (CVG-HR-CS QTAAS), respectively the validation of a general method with wide applicability at least for the analysis of foods of plant and animal origin, environmental samples (soil, water sediments and sludge from the residual water treatment stations) and recyclable (bio)plastic materials. In the case of the (bio)plastic materials, besides the As, Sb, Bi and Hg content, the Mn, Cu, Cd, Ni, Cr, Co, Pb and Zn content was also evaluated by HR-CS FAAS, which are present in these materials because of the contamination or the addition of additives during the technologic process of the synthesis and processing to final products, some of them being restricted to be used in accordance with the Directive 2002/95/CE, or even prohibited to be used, especially in (bio)plastics used in packaging of foods and drinks. It was intended to evaluate the (bio)plastic materials because these were and are currently used, respectively recycled by circular economy in huge amounts. Additionally, the lifetime of the plastic materials is very long (at least 25–50 years), being produced and used before the introduction of restrictions concerning the use of inorganic additives. There is a very wide range of (bio)plastics, which differ both in terms of the base polymer and the envisaged range of use and recycling, and, therefore, the knowledge of their chemical composition is important, from the perspective of the toxic element content, in order to ensure the maximum safety conditions during the selective recycling.

In the development stage of the HR-CS QTAAS method, all the stages of the optimization and analytical characterization were covered in the research methodology, including comparison with other methods. In case of (bio)plastic materials, taking into account the diversity of polymers and their chemical composition, the differences between the content of elements depending on the nature of the polymer and the provenience of the recycled materials were emphasized by statistical tests.

## **Chapter 1. High-Resolution Continuum Source Atomic Absorption Spectrometry versus Line Source Atomic Absorption Spectrometry**

### **1.1. Short History of the Atomic Absorption Spectrometry**

Although the absorption phenomenon of the optical radiations has long been known, the atomic absorption spectrometry (AAS) was recognised as analytical laboratory method only in 1955.<sup>1</sup> The obstacle of the AAS method's transfer from research or academic laboratories to routine analysis laboratories was due to the lack of an adequate primary source which could ensure a particular sensitivity of the method in case of a low-resolution monochromator which was known at that time. For the first time, Sir Alan Walsh proposed the use of specific primary source for the radiation of the sample, namely the hollow cathode lamp (HCL), when using the low-resolution monochromator equipped with a photomultiplier tube (PMT) as detector of the specific resonance radiation absorbed by the atomic population.<sup>2</sup> The first atomic absorption spectrometers were the ones with flame (FAAS), then those using graphite furnace (GFAAS) appeared in 1974.<sup>3</sup>

### **1.2. Appearance of the High-Resolution Continuum Source Atomic Absorption Spectrometry as Alternative to the Onewith Line Source**

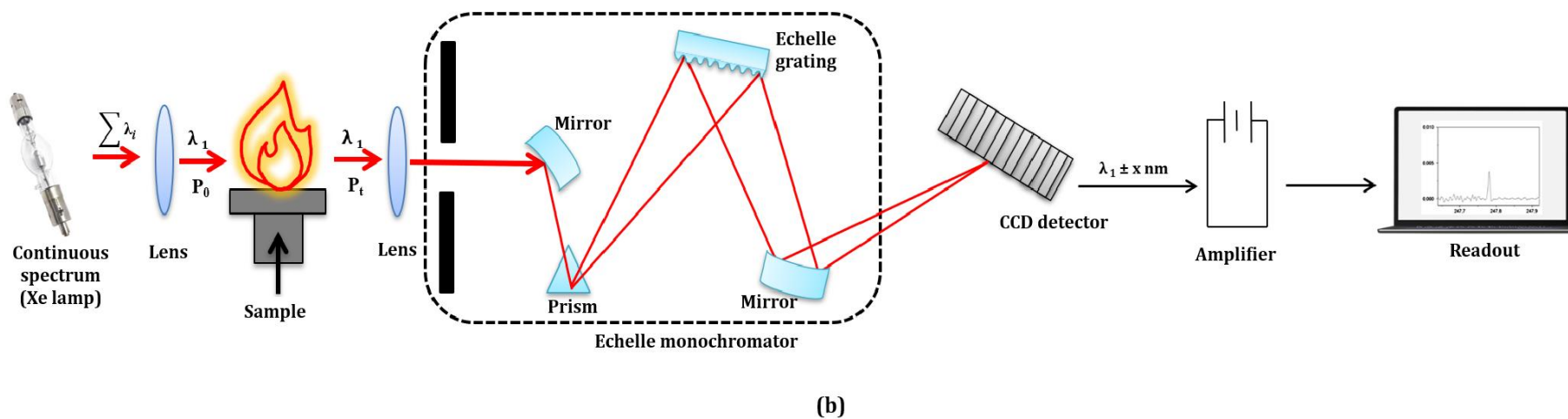
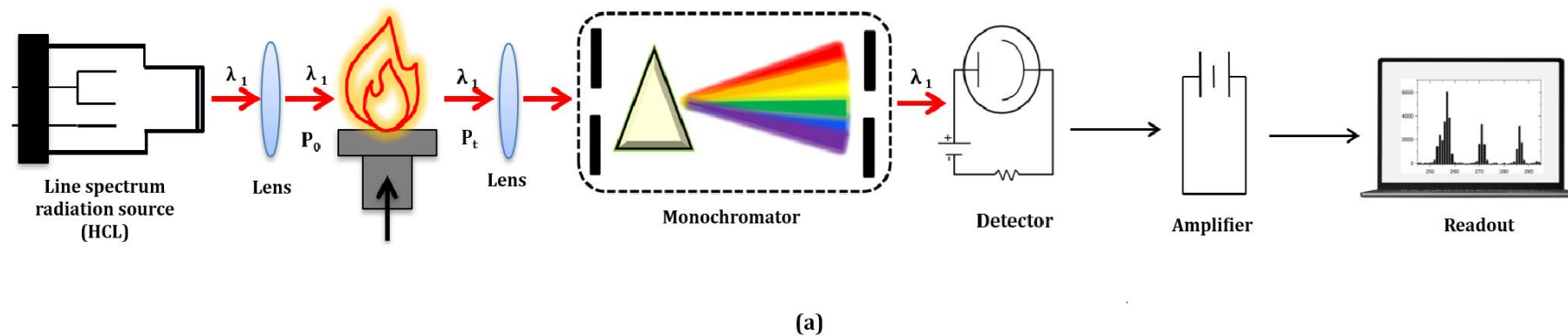
Atomic absorption is distinguished by two main characteristics: high sensitivity and selectivity. The high sensitivity of the atomic absorption results from the fact that the most atoms are on the essential energy level at the flame temperature, and, therefore, the probability of the radiation absorption by the atoms is high, compared with the radiation emission by excitation, while the selectivity is ensured by the fact that the atoms absorb and emit only their specific radiations, respectively by the use of specific radiation sources.<sup>4</sup> Two analysis methods by atomic absorption were developed: (i) low-resolution atomic absorption spectrometry with line source in flame or graphite furnace (LR-LS FAAS, LR-LS GFAAS); (ii) high-resolution atomic absorption spectrometry with continuous spectrum source in flame or graphite furnace (HR-CS FAAS, HR-CS GFAAS).<sup>4</sup>

Helmut Becker-Ross was the first who proposed that the AAS method retains its selectivity by the use of a continuous spectrum source but in order to increase sensitivity, the use of a high-resolution monochromator is required, which is able to provide a spectral bandwidth of about 2 pm, similar with the width of the spectral lines.<sup>5</sup> In 1996, together with his team from the Institute of Spectrochemistry and Applied Spectroscopy (ISAS) of Berlin, he proposed fully novel concept of the HR-CS AAS instrument<sup>6</sup> that eliminated the significant disadvantages of the

LS-AAS concept, such as: (i) the use of monoelemental hollow cathode lamps (HCL) or electrodeless discharge lamps (EDL); (ii) low versatility for the selection of the analysis wavelength; (iii) the necessity of the change of lamps for each element; (iv) long time of analysis.<sup>7</sup> The HR-CS AAS instrumental concept proposed by the team of Becker-Ross was transferred to the Analytik Jena company from Germany, which launched on the market the first commercial model of HR-CS FAAS with acetylene-air flame (ContrAA 300) in 2004.<sup>5,8</sup> In Romania, the first ContrAA300 commercial model with flame and quartz tube purchased by a university was within the Babeş-Bolyai University in 2007, on which the research of the present PhD thesis was carried out. At the moment, Analytik Jena produces equipments within the ContrAA 800 family, in various flexible configurations with flame, graphite furnace, quartz tube, and direct analysis mode of solid samples, being the only existing worldwide trader.<sup>9</sup>

### **1.3. Comparison between the Low-Resolution Line Source Atomic Absorption Spectrometry (LR-LS AAS) and the High-Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS)**

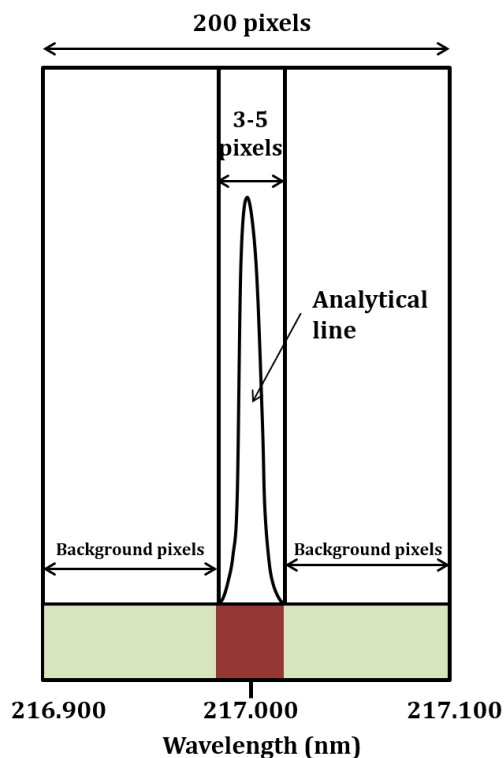
The appearance of the commercial HR-CS AAS instrumental technology represented a turning point, almost completely capturing the interest, detrimental to the traditional LR-LS AAS method. The fundamental differences the two technologies and their operating principles are depicted in Fig. 1.1. Significant differences: in case of the HR-CS AAS technology a single, continuous spectrum Xe lamp is used for the fast sequential analysis of all elements and a high-resolution echelle monochromator, equipped with a CCD detector for the recording and display of the spectrum on a range at most  $\pm 1$  nm, around the analytical line, in comparison with the classical LR-LS AAS technology which uses a set of HCL and EDL lamps for the analysis of the elements, a low-resolution monochromator equipped with photomultiplier and the measurement of the signal on the peak of the analytical line without the visualization of the spectral environment around the analytical line. Additionally, the HR-CS AAS technology allows the integration of the analytical signal on the analytical line, depending on the number of pixels ( $CP \pm n$ , where  $n = 1, 2, 3$  is the number of pixels, against the central one on which the signal is integrated), which ensures the significant increase of the sensitivity, compared with the LR-LS AAS technology, which allows the measurement just at the central pixel of the line.<sup>10,11</sup>



**Fig. 1.1.** Operating principle of the classical LR-LS FAAS instrumental technology with hollow cathode lamp (a) and the unconventional HR-CS FAAS technology with Xe lamp (b)

The HR-CS AAS instrumental technology ensures also the selectivity of the method, even if the continuous radiation emitted by the Xe lamp passes simultaneously by the atomization source, where there are atoms on the fundamental level of the element from the sample, because the absorption is selective, as each element absorbs only the corresponding radiations, in accordance with the electronic structure, without spectral interferences. On the other hand, in case of the LR-LS AAS technology, the selectivity is ensured by the change of the HCL lamp.<sup>4</sup>

By combining the double echelle monochromator (DEMON), which uses a Littrow prism and an echelle grid, with a CCD detector, specifically designed for spectral applications, the HR-CS AAS technology allows the recording of absorption spectra with high-resolution (2 pm), without spectral interferences and obtaining a high sensitivity, on a wide spectral range (190 – 950 nm), compared with the classical LR-LS AAS technology.<sup>6,7</sup> The HR-CS AAS technology provides more possibilities for the measurement of the signal compared with LR-LS AAS: (i) measuring on the peak of the spectral line, similarly with LR-LS AAS; (ii) signal–wavelength 2D integration; (iii) signal–wavelength–time 3D integration, which are determined by the operating principle of the CCD.<sup>2,5,11</sup> A higher signal can be obtained by these ways of measurement, which improve the sensitivity and limits of detection (LOD). The HR-CS AAS technology is much more advanced with respect to the background correction, whose principle can be observed in Fig. 1.2., because it performs a simultaneous background correction together with the measurement of the signal at the analytical line.



**Fig. 1.2.** Signal measurement and the simultaneous background correction in the HR-CS AAS technology<sup>5</sup>

Additionally, allows the fine structure of the background correction, as a result of the presence of the molecular bands of NO, OH, etc. in the UV range. This correction is not possible within the LR-LS AAS technology.<sup>10,12</sup>

#### **1.4. Applications of the HR-CS AAS Analytical Technology**

The same types of atomizers and sample introduction systems are used both in HR-CS AAS and LR-LS AAS. The practical success of the much more sensitive HR-CS AAS analytical technology, compared to the LR-LS AAS, was demonstrated by the successful use in monoelemental and multielemental analysis, in various types of samples, such as foods, biomass samples and ash resulted from incineration, pharmaceutical products, atmospheric particles, environmental samples, petroleum and petrochemical products, polymers, glass, coal and soot, nanocomposites and biological samples. The diversity of the fields clearly illustrates the robustness and the outstanding performance of the HR-CS AAS with flame and graphite furnace analytical technology on various matrices.<sup>7</sup>

##### **1.4.1. Applications of the HR-CS FAAS Analytical Technology**

The HR-CS FAAS method is mainly used for the determination of metals. The analytical methods are either monoelemental but mostly multielemental, due to the fact that a single continuous spectrum Xe lamp is used for the determination of all elements, which significantly reduces the time of analysis and acetylene consumption. In case of multielemental analyses, the determinations are carried out under optimal conditions because the instrument allows the automatic selection of the of the optimal operating conditions, namely the automatic and fast change of the optimal wavelength, burner height and acetylene and air flow, when passing from an element to another.<sup>13</sup> The literature data highlight the superiority of HR-CS FAAS against LR-LS FAAS, in terms of faster operating, fast and advanced background correction, the versatility of choosing the primary and secondary wavelengths of the elements, LODs and better precision.<sup>14</sup> Numerous research address the problem of the LODs' improvement by the integration of the signal depending on the number of pixels, and the elimination of interferences, either by the possibilities offered by the instrument's software (e.g., fine structure background correction of the molecular bands over the analytical lines in UV range), or internal standard method.<sup>15</sup> A particular interest is given to the sample preparation and preconcentration methods by (micro)extraction (on solid phase or liquid-liquid).<sup>16-30</sup> In case of environmental samples the HR-CS FAAS was applied, without preconcentration, with superior results compared to ICP-OES, both in terms of accuracy and LODs.<sup>31-33</sup>



### 1.4.2. Applications of the HR-CS GFAAS Analytical Technology

Altogether, a number of 28 elements were measured using the HR-CS GFAAS technique, of which Fe, Ni, Cd and Co were the most frequently analysed. The simultaneous multielemental analyses were usually focused on two elements which have spectral lines in the same window but the possibility of the determination of three or four elements was also studied.<sup>34</sup> Numerous studies' purpose was the comparison of the analytical performance of the HR-CS GFAAS technique with the conventional LR-LS GFAAS technique. Numerous studies were focused on the optimization of the HR-CS GFAAS method, in order to ensure the most precise measurements of the analytes and an efficient multielemental analysis. In the case of As and Se determination by HR-CS GFAAS, difficulties were encountered due to the spectral interferences with diatomic molecules, resulted in the graphite furnace, such as PO, CS, NO or SiO.<sup>34</sup> Significant limitations were observed in case of the LR-LS GFAAS method, therefore, the HR-CS GFAAS technique is much more efficient and attractive and offers a larger dynamic range of the calibration curves, a better sensitivity, este mult mai eficientă și atractivă și oferă un domeniu dinamic mai larg al curbelor de etalonare, o sensibilitate mai bună, besides improved values of LODs, precision and accuracy.<sup>35</sup>

The HR-CS GFAAS instrumentation is widely applied, both for sequential<sup>36,37</sup> and simultaneous multielemental analysis.<sup>38-45</sup> In case of simultaneous analysis, the advantage of the use of secondary line of the elements, together with the main ones, was exploited.<sup>38-44,46</sup> Besides simultaneous analysis, one of the great benefits of the HR-CS GFAAS technique is the direct determination from solid, without any work-up of the sample,<sup>39,43,44,47</sup> however, several methods were developed for the prereduction of the analyte, followed by its extraction by various procedures.<sup>40,45,48-50</sup>

### 1.4.3. Applications of the HR-CS QTAAS Analytical Technology

The quartz tube atomizer (QTA) was used at least for 20 years, preferred for the atomization of analytes which generate gaseous species following chemical derivatization to chemical vapors (CVG) (hydrides and cold vapors of Hg).

Numerous research were focused on the improvement of this atomization method, especially concerning the elimination of spectral interferences of the gaseous concomitants (e.g., NO<sub>x</sub>).<sup>51-53</sup> HR-CS QTAAS allows the determination of chemical vapor generating elements, providing advantages over the traditional technologies with line source and various atomizers, such as QTA, GFAAS, etc. Preconcentration procedures of the samples are applied, for the increase of the sensitivity and improvement of LODs, or procedures based on SPME, on various

nanostructured supports.<sup>54–57,60–62,67,70,71,74</sup> Being more and more often used, in case of GFAAS, the *in-situ* collection of hydrides on the wall of the graphite furnace is applied, followed by atomization and signal measurement.<sup>55</sup> With respect to the character of applications, the multielemental analysis methods can be noted, in the case of analytical technology with continuous spectrum source, in comparison with the traditional monoelemental technologies with line source, regardless the type of the atomizer (quartz tube, graphite furnace or DBD).<sup>54,56,58,59,63–65,68,69,72–76</sup> With respect to LODs, it was observed that the HR-CS QTAAS or HR-CS GFAAS technology ensures better values in most cases, compared with the classical technologies with line source.

## **Chapter 2. Determination of As, Sb, Bi, Hg, Se and Te in Food and Environmental Samples by High-Resolution Continuum Source Quartz Tube Atomic Absorption Spectrometry and Chemical Vapor Generation**

### **2.1. Situation at International Level. Working Hypothesis and Research Objectives**

Although the CVG and UV-PVG methods offer a remarkable sensitivity and separation of the analytes from the sample matrix, the derivatization procedure to chemical vapors is still affected by the non-spectral interferences, coming from the nitrate anion, but mostly from the nitrite, resulted from the  $\text{HNO}_3$  with  $\text{HCl}$  and  $\text{H}_2\text{O}_2$  mixture, in the digestion and/or derivatization stage, regardless the measurement method, but also by the spectral and background interferences, from the nitrogen oxides, oxygen and water molecules, which especially affect the As and Se determination by AAS.<sup>55,78-83</sup> The nitrite and  $\text{NO}_x$  have a severe depressive effect on the hydride generation and thus on the analytical sensitivity, resulting not only non-spectral interferences in liquid phase but also a high and noisy background signal, which compromises the analysis.<sup>55,78-83</sup> Several reagent were studied for the chemical decomposition of  $\text{NO}_2^-$ , before derivatization to chemical vapors, of which the sulfamic acid was proved to be the most efficient.<sup>79-82</sup>

The considered working hypothesis for the development and validation of the CVG-HR-CS QTAAS method were the following: (i) an efficient elimination of both non-spectral and spectral interferences of the concomitants, so that the method would be sufficiently selective and present a general applicability for the determination of As, Sb, Bi, Hg, Se and Te, regardless the composition of the analytical matrix; (ii) the method would ensure an adequate sensitivity, in comparison with other methods used in laboratories, so that it could be applied at least on food and environmental samples, at concentrations below the maximal permitted values, with respect to the terms of the European legislation; (iii) the results should be of wide interest for the academic community and social environment, so that the results and analytical procedures could be transferred on other instrumentations also, in other laboratories.

### **2.2. Materials and Method**

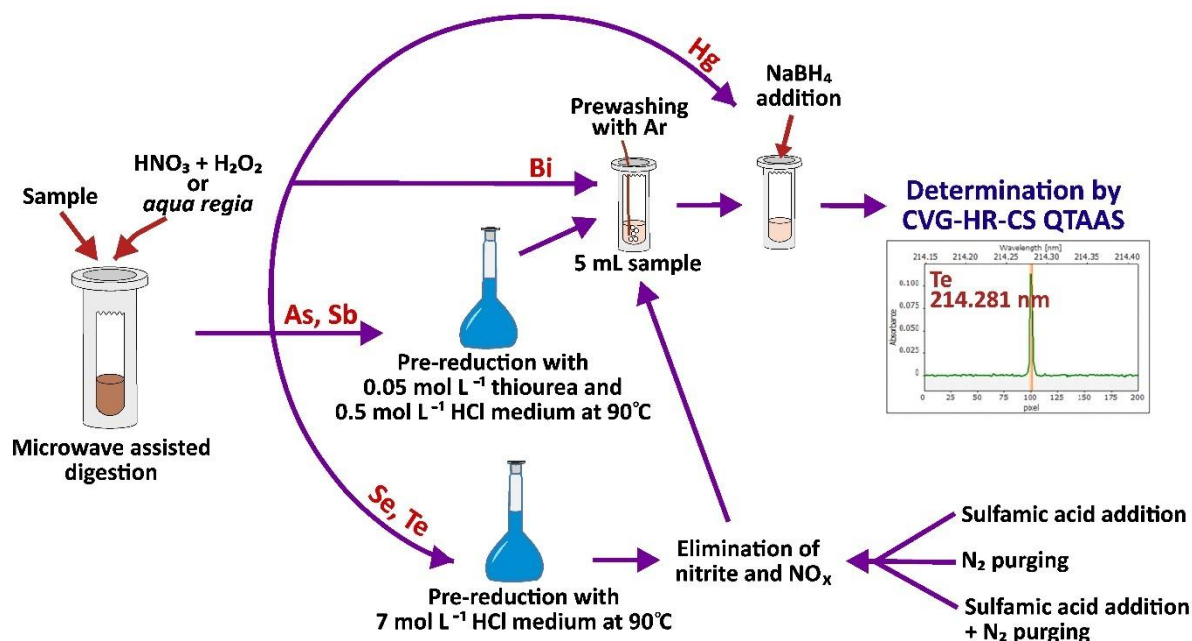
#### **2.2.1. CVG-HR-CS QTAAS Instrumentation**

The determinations were carried out on the CVG-HR-CS QTAAS equipment, which includes a ContrAA 300 high-resolution atomic absorption spectrometer, Analytik Jena (Jena, Germany), equipped with a CCD detector, a HS55 discontinuous system for the chemical vapor



### 2.2.2. Sample Preparation

A presentation of the principle of sample preparation is depicted in Fig. 2.2.<sup>85</sup>



**Fig. 2.2.** Scheme of the principle of sample preparation procedure for the determination of As, Sb, Bi, Hg, Se and Te by the CVG–HR–CS QTAAS method<sup>85</sup>

The sample preparation included the microwave-assisted digestion using  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  for the biological samples, and the  $\text{HNO}_3$  and HCl mixture for the soil, sludge and sediment samples. The samples were filtered and diluted for analysis. The prereduction with thiourea was applied for As and Sb, respectively concentrated HCl for Se and Te, followed by the derivatization to chemical vapors. The concentrations in the final solution were determined, for As and Sb, in  $0.5 \text{ mol L}^{-1}$  HCl and  $0.05 \text{ mol L}^{-1}$  thiourea medium, respectively  $7 \text{ mol L}^{-1}$  HCl for Se and Te. The prereduction was not necessary in case of Bi and Hg, and derivatization was conducted in a HCl medium of  $0.5 \text{ mol L}^{-1}$ . The details of the sample preparation procedure can be found in the reference.<sup>85</sup>

### 2.2.3. Validation of the CVG–HR–CS QTAAS Method

The CVG–HR–CS QTAAS method was validated by the evaluation of the analytical performance, namely the instrumental LODs, the real sample LODs, accuracy (recovery and precision) and linearity of the calibration curves, using the WIA procedure for the acquisition of the absorption signals. The instrumental LODs were determined based on the  $3\sigma$  criterion ( $\text{LOD} = 3s_b/m$ , where  $s_b$  is the standard deviation of the signal of the blank sample, for  $n = 11$

measurements, and  $m$  is the slope of the calibration curve). The LODs of the method were expressed in  $\text{mg kg}^{-1}$  in real samples. The accuracy of the method was evaluated by the analysis of several CRM samples and fortified samples of  $5 \mu\text{g L}^{-1}$  analyte concentration, by recovery and extended laboratory uncertainty, for  $n = 3$  parallel measurements and a confidence level of 95 %, by which the presence of systematic errors was verified. The performance of the method was evaluated by using the  $z'$  or  $z$  score, and the precision was expressed as percentage relative standard deviation (RSD%), based on the combined laboratory uncertainty ( $u_{\text{c-lab}}$ ).<sup>85</sup>

## 2.3. Results and Discussion

### 2.3.1. Optimization of the Prereduction and CVG Conditions for the Determination of As, Sb, Hg, Bi, Se and Te with CVG–HR–CS QTAAS

The CVG–HR–CS QTAAS method has been optimized with respect to the HCl, thiourea,  $\text{NaBH}_4$ , NaOH concentrations and the volume of  $\text{NaBH}_4$  solution added in a 5 mL aliquot volume of sample. The optimum working conditions are presented in Table 2.1.<sup>85</sup>

**Table 2.1.** Optimum working conditions for the determination of As, Sb, Hg, Bi, Se and Te by CVG–HR–CS QTAAS<sup>85</sup>

Parameter	Setting		
	Hg	As, Bi, Sb	Se, Te
Analytical wavelength (nm)	253.652 Hg	193.696 As, 223.061 Bi, 217.582 Sb	196.027 Se, 214.281 Te
Transient signal measurement	Height	Height	Height
Number of pixels associated to WIA signal	5 (CP $\pm$ 2)	5 (CP $\pm$ 2)	5 (CP $\pm$ 2)
QTA temperature ( $^{\circ}\text{C}$ )	$150 \pm 10$	$950 \pm 10$	$950 \pm 10$
Ar flow rate ( $\text{L h}^{-1}$ )	6	6	6
Spectrum recording time (s)	10	10	10
Prewashing time of reaction cell and QTA with Ar before $\text{NaBH}_4$ solution addition (s)	0	20 As 20 Bi 30 Sb	20 Se 20 Te
Purging time with Ar of the reaction cell after $\text{NaBH}_4$ solution addition (s)	25	25	25
Aliquot sample volume (mL)	5	5	5
HCl concentration in aliquot sample ( $\text{mol L}^{-1}$ )	0.5	0.5	7
Thiourea concentration in aliquot sample ( $\text{mol L}^{-1}$ )	–	0.05	–
Volume of $\text{NaBH}_4$ solution (mL)	3.5	2	3.5
$\text{NaBH}_4$ concentration (% m/v)	2.5	2.5	2.5
NaOH concentration (% m/v)	0.1	0.1	0.1

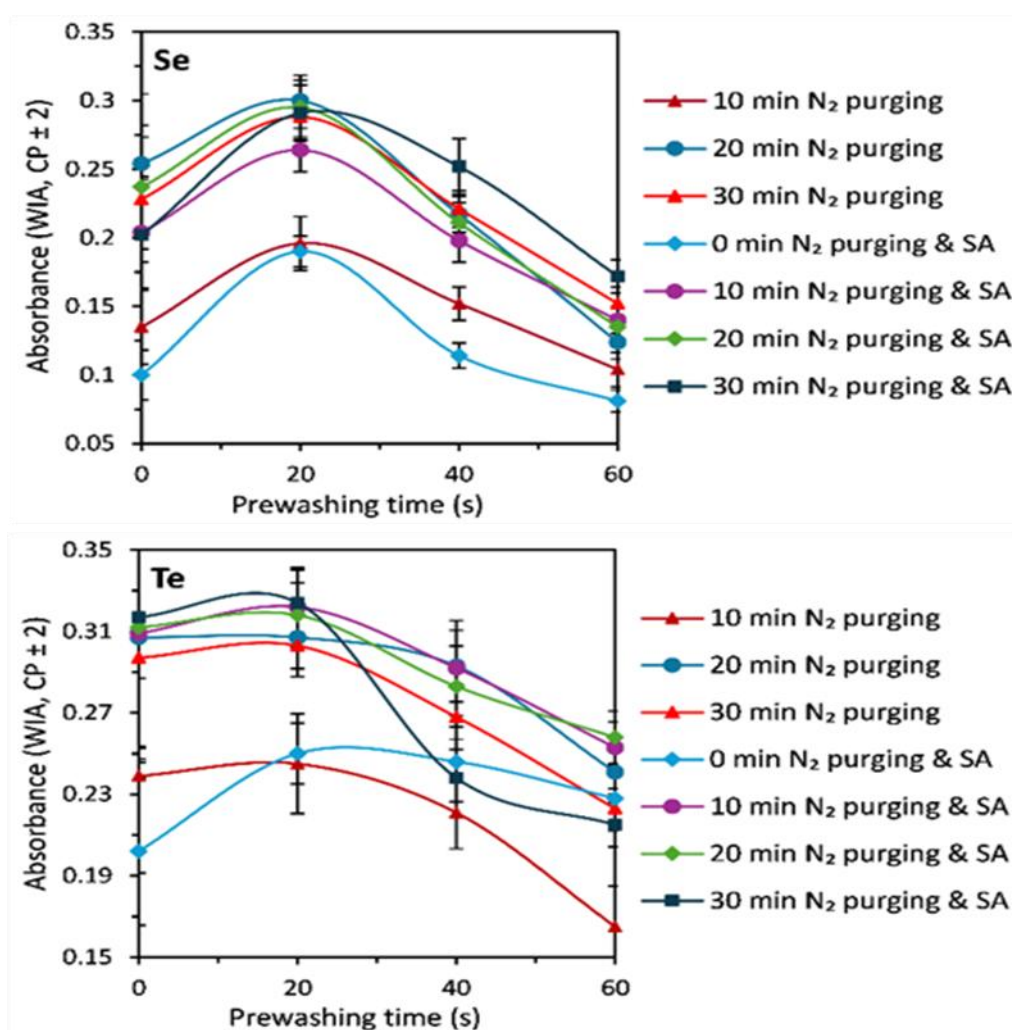
### 2.3.2. Elimination of the Nitrite, NO<sub>x</sub> and O<sub>2</sub> Interferences for the Determination of Se, Te, As, Sb and Bi by CVG–HR–CS QTAAS

Three procedures for the elimination of the interferences caused by the nitrite and NO<sub>x</sub> were investigated, in the determination of Se and Te in presence of 10% (v/v) HNO<sub>3</sub>, in synthetic samples with a concentration of  $10 \mu\text{g L}^{-1}$  Se(VI) and Te(VI). During the first procedure, 5 mL 10% (m/v) solution of sulfamic acid was added after the prereduction step of Se(VI) and Te(VI), by heating in a water bath with  $7 \text{ mol L}^{-1}$  HCl. In the second procedure, the previously obtained solution was subjected to a supplementary Ar purging, for a period of 10–30 min at room temperature. During the third procedure, a simple Ar purging was applied for 10–30 min, after prereduction, without the addition of sulfamic acid. After the evaluation of the performance of the three procedures, these were applied for the determination of Se and Te in CRM samples and real samples, by external calibration, using standard solutions in  $7 \text{ mol L}^{-1}$  HCL medium, without HNO<sub>3</sub> addition.<sup>85</sup>

The variation of the absorption signal ( $\text{CP} \pm 2$  pixels) for Se and Te in synthetic samples after decomposition of the nitrite with sulfamic acid with or without Ar purging, for 10–30 min, after the prereduction stage, is presented in Fig. 2.3.<sup>85</sup> The influence of the prewashing time (0–60 s) of the reaction cell and QTA with  $6 \text{ L h}^{-1}$  Ar, before the addition of NaBH<sub>4</sub>, was studied in all cases. The recorded spectra and the transient signal for Se and Te under different working conditions are presented in Fig. 2.4.–2.7.<sup>85</sup> The determination of Se and Te could be possible by the nitrite decomposition with 1% (m/v) sulfamic acid solution, without the purging of the sample with nitrogen and with/without prewashing of the reaction cell and QTA with Ar (Fig. 2.4. a,b and Fig. 2.6. a,b).<sup>85</sup> It was observed the addition of sulfamic acid before prereduction did not provide the desired result, with respect to the overcoming of the depressive non-spectral interferences on Se and Te. The results are in accordance with the literature data, which indicate the fact that the nitrite has a stronger depressive effect than the nitrate.<sup>79</sup> In addition, the absorption signal of Se and Te could be measured without interferences by the purging of the solution N<sub>2</sub> for 20 min and with/without prewashing the reaction cell and QTA with Ar for 20 s (Fig. 2.5. c,d and Fig. 2.7. c,d), without the addition of 1% (m/v) sulfamic acid.<sup>85</sup> The prewashing of the reaction cell and QTA with Ar for 20 s had a critical influence, in any case, not only on the absorption signal but mostly on the noise of the background signal, as it can be observed in the spectra presented in Fig. 2.4.–2.7. b,d.<sup>85</sup>

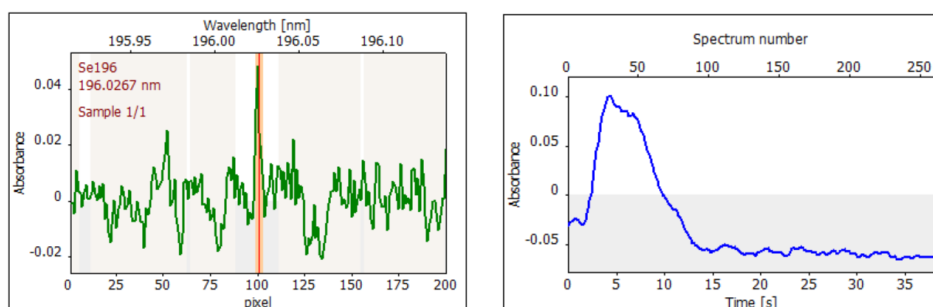
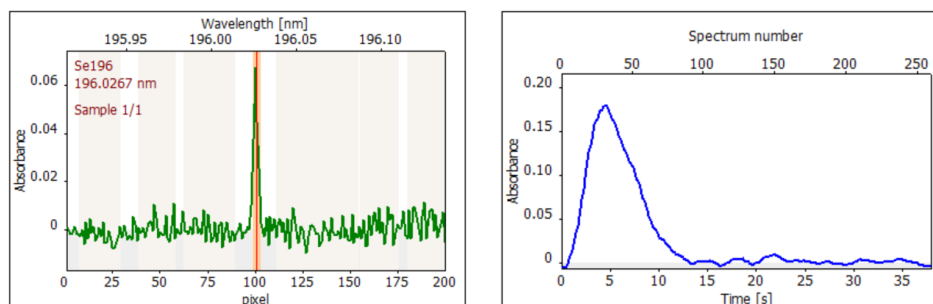
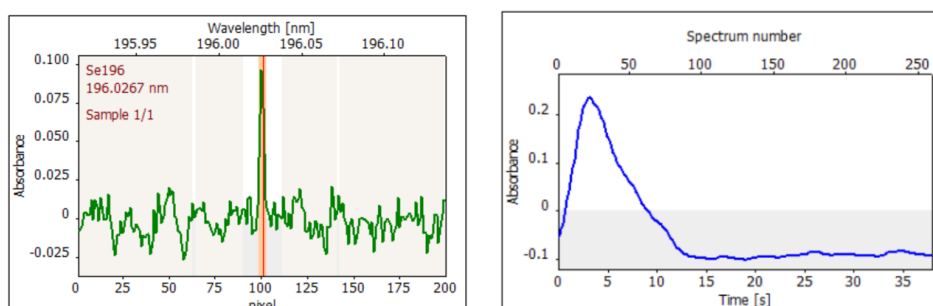
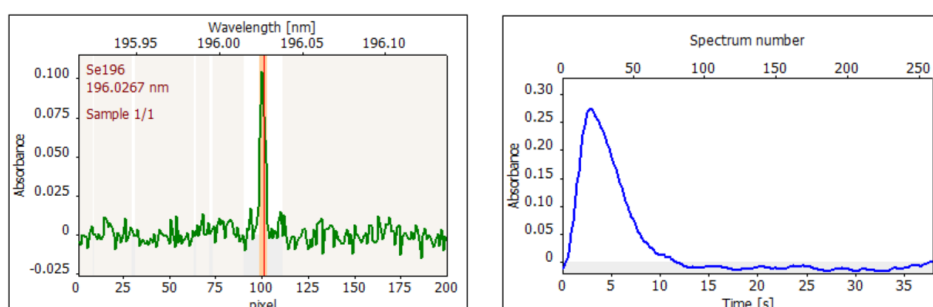
The results have shown that the best method for the elimination of the interferences for Se and Te was the purging with nitrogen, for 20 min, after the prereduction and washing of the reaction cell and QTA with argon for 20 s, before the addition of NaBH<sub>4</sub> solution. The addition of sulfamic acid and purging with nitrogen for 10 min improved the sensitivity as well, for Se and

Te.<sup>85</sup> However, the nitrogen purging of the solution for 20 min without sulfamic acid addition, respectively purging for 10 min and addition of 1% (m/v) sulfamic acid ensured 1.3–1.6 times better sensitivity for the determination of Se and Te, compared with the procedure based on sulfamic acid addition only.<sup>85</sup> The decrease of the signal for Se and Te at prewashing times of the reaction cell for more than 20 s, indicates that the presence of trace amounts of oxygen in the atomization cell is an essential support for the efficient atomization of hydrides, alongside hydrogen.<sup>85</sup> Nitrogen purging or sulfamic acid addition was not necessary in the case of As, Sb and Bi determination, but the washing of the reaction cell and QTA with argon was essential, for the elimination of residual NO<sub>x</sub>. In case of Hg, neither prereduction, nitrogen purging of the sample, respectively prewashing of the reaction cell and QTA with Ar was necessary, before the addition of borohydride solution.<sup>85</sup>

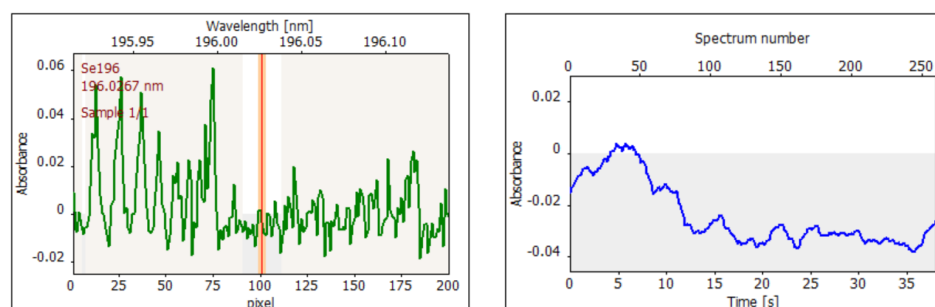


**Fig. 2.3.** The variation of the absorption signal for Se 196.027 nm and Te 214.281 nm under different pretreatment conditions of the sample in 7 mol L<sup>-1</sup> HCl and 10% (v/v) HNO<sub>3</sub> medium, after the prereduction stage and different prewashing times of the reaction cell and QTA before the addition of NaBH<sub>4</sub> solution<sup>85</sup>

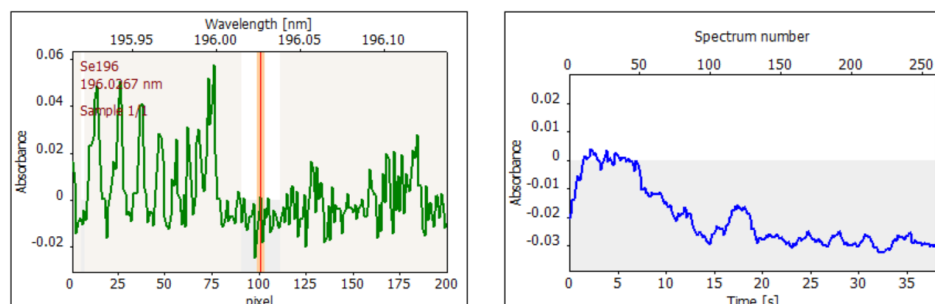


(a) Without N<sub>2</sub> purging and without prewashing of the reaction cell with Ar(b) Without N<sub>2</sub> purging and with prewashing of the reaction cell with Ar for 20 s(c) Purging with N<sub>2</sub> for 10 min and without prewashing of the reaction cell with Ar(d) Purging with N<sub>2</sub> for 10 min and with prewashing of the reaction cell with Ar for 20 s

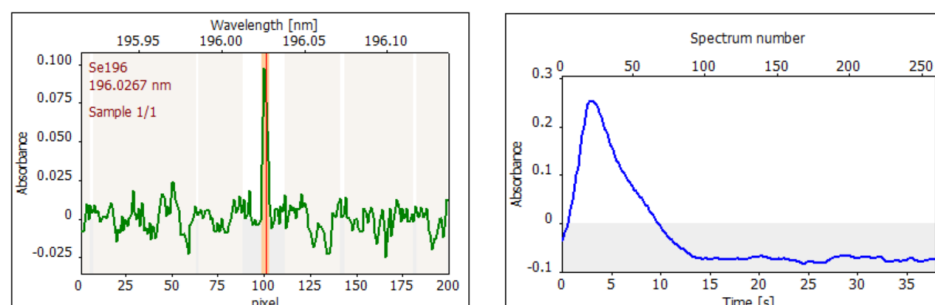
**Fig. 2.4.** Absorption signals obtained for a 5 mL aliquot volume of sample of 10  $\mu\text{g L}^{-1}$  Se in the presence of 10% (v/v) HNO<sub>3</sub> in 7 mol L<sup>-1</sup> HCl and 1% (m/v) sulfamic acid added for the decomposition of nitrite under different sample preparation conditions after prereduction of Se(VI) to Se(IV) (with/without purging of the solution with N<sub>2</sub> and with/without prewashing of the reaction cell and QTA with Ar)<sup>85</sup>



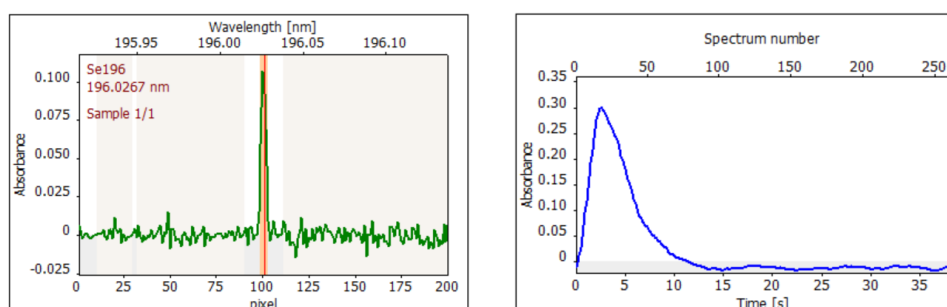
(a) Without N<sub>2</sub> purging and without prewashing of the reaction cell with Ar



(b) Without N<sub>2</sub> purging and with prewashing of the reaction cell with Ar for 20 s

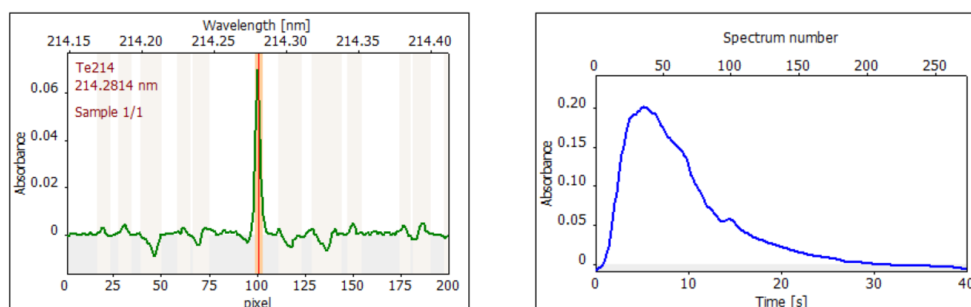
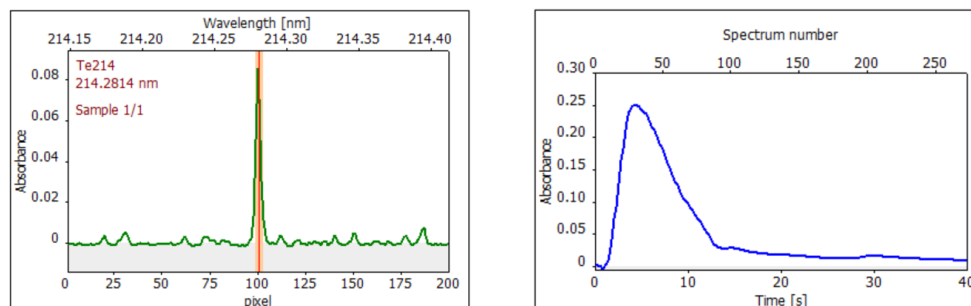
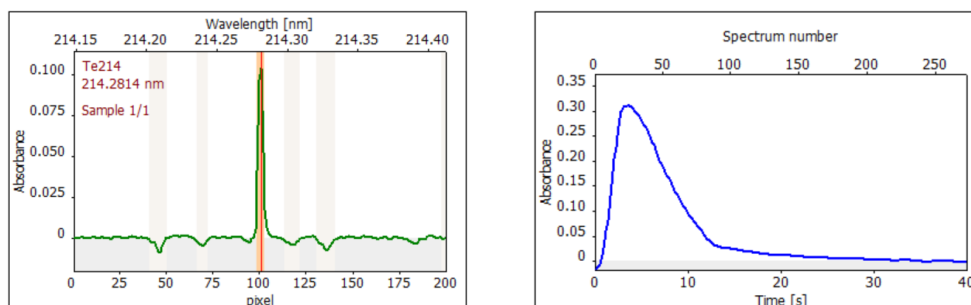
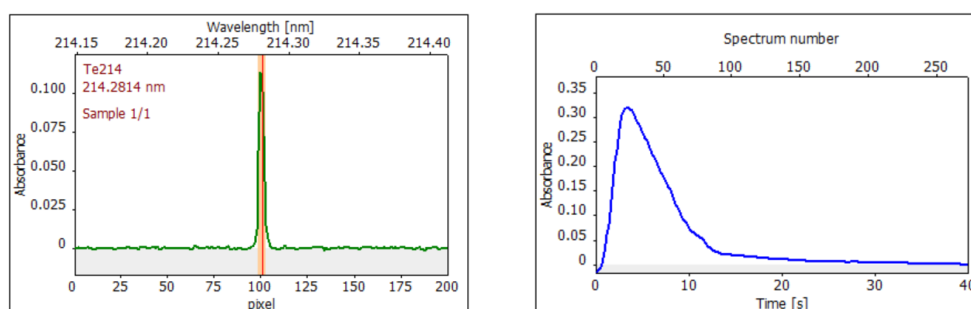


(c) Purging with N<sub>2</sub> for 20 min and without prewashing of the reaction cell with Ar

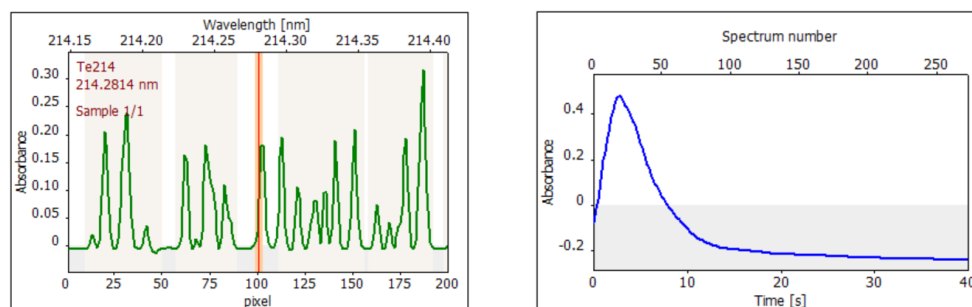


(d) Purging with N<sub>2</sub> for 20 min and with prewashing of the reaction cell with Ar for 20 s

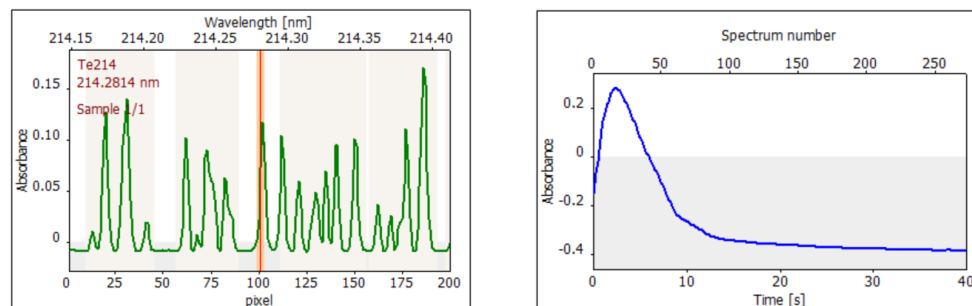
**Fig. 2.5.** Absorption signals obtained for a 5 mL aliquot volume of sample of 10  $\mu\text{g L}^{-1}$  Se in the presence of 10% (v/v) HNO<sub>3</sub> in 7 mol L<sup>-1</sup> HCl without sulfamic acid under different sample preparation conditions after prereduction of Se(VI) to Se(IV) (with/without purging of the solution with N<sub>2</sub> and with/without prewashing of the reaction cell and QTA with Ar)<sup>85</sup>

(a) Without N<sub>2</sub> purging and without prewashing of the reaction cell with Ar(b) Without N<sub>2</sub> purging and with prewashing of the reaction cell with Ar for 20 s(c) Purging with N<sub>2</sub> for 10 min and without prewashing of the reaction cell with Ar(d) Purging with N<sub>2</sub> for 10 min and with prewashing of the reaction cell with Ar for 20 s

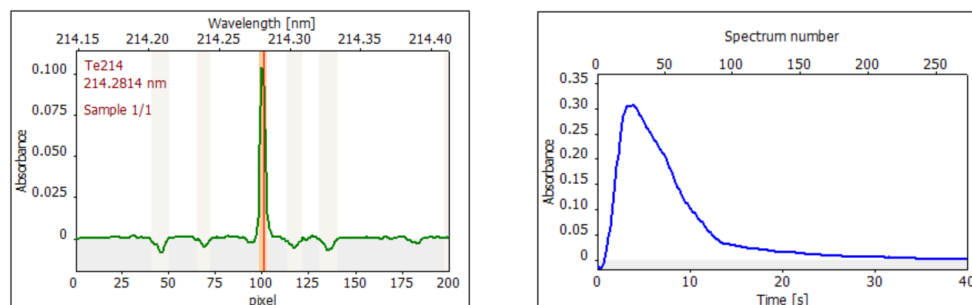
**Fig. 2.6.** Absorption signals obtained for a 5 mL aliquot volume of sample of 10  $\mu\text{g L}^{-1}$  Te in the presence of 10% (v/v) HNO<sub>3</sub> in 7 mol L<sup>-1</sup> HCl and 1% (m/v) sulfamic acid added for the decomposition of nitrite under different sample preparation conditions after prereduction of Te(VI) to Te(IV) (with/without purging of the solution with N<sub>2</sub> and with/without prewashing of the reaction cell and QTA with Ar)<sup>85</sup>



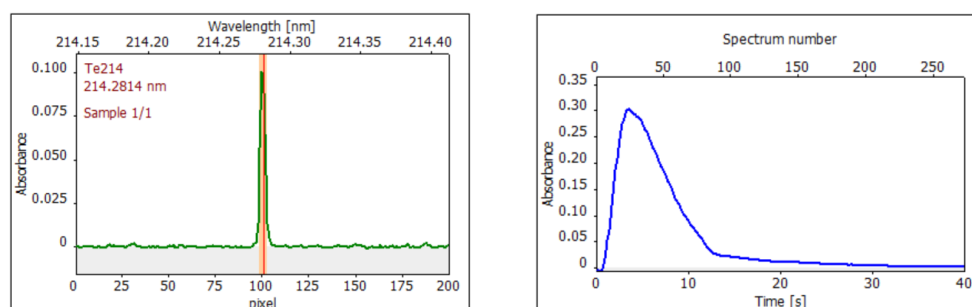
(a) Without N<sub>2</sub> purging and without prewashing of the reaction cell with Ar



(b) Without N<sub>2</sub> purging and with prewashing of the reaction cell with Ar for 20 s



(c) Purging with N<sub>2</sub> for 20 min and without prewashing of the reaction cell with Ar

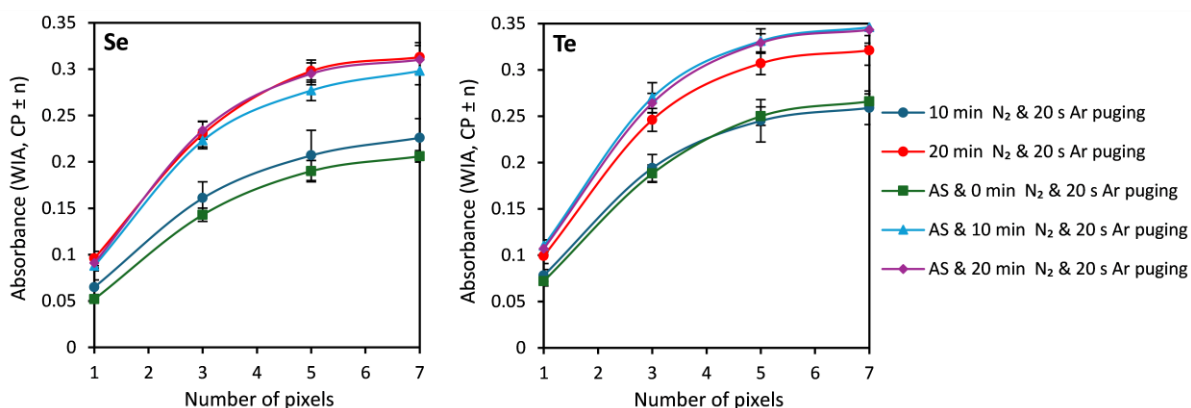


(d) Purging with N<sub>2</sub> for 20 min and with prewashing of the reaction cell with Ar for 20 s

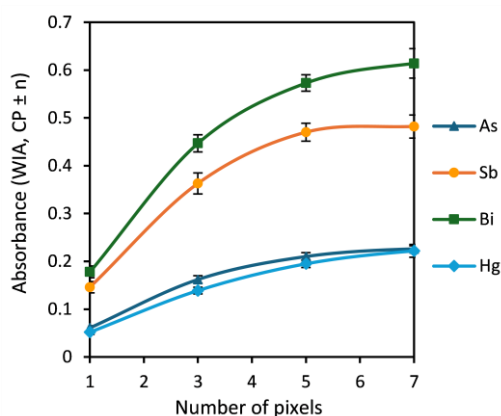
**Fig. 2.7.** Absorption signals obtained for a 5 mL aliquot volume of sample of 10  $\mu\text{g L}^{-1}$  Te in the presence of 10% (v/v) HNO<sub>3</sub> in 7 mol L<sup>-1</sup> HCl without sulfamic acid under different sample preparation conditions after prereduction of Te(VI) to Te(IV) (with/without purging of the solution with N<sub>2</sub> and with/without prewashing of the reaction cell and QTA with Ar)<sup>85</sup>

### 2.3.3. Calibration Curves and LODs in the CVG–HR–CS QTAAS Method

The variation of the WIA signal depending on the number of pixels in optimum conditions for the three procedures used for the elimination of the interferences of nitrite and  $\text{NO}_x$  in the determination of Se and Te by CVG–HR–CS QTAAS is presented in Fig. 2.8., while for As, Sb and Bi with the prewashing of the reaction cell and QTA and Hg without prewashing with Ar is presented in Fig. 2.9.<sup>85</sup>



**Fig. 2.8.** Influence of the pixels' number on the WIA signal for a 5 mL aliquot volume of sample of  $10 \mu\text{g L}^{-1}$  Se and Te registered under different sample preparation conditions after prereduction in  $7 \text{ mol L}^{-1}$  HCl and in presence of 10% (v/v)  $\text{HNO}_3$  ( $\text{CP} \pm n$ ;  $n = 1, 2, 3$ )<sup>85</sup>



**Fig. 2.9.** Influence of the pixels' number on the WIA signal for a 5 mL aliquot volume of sample of  $10 \mu\text{g L}^{-1}$  As and Sb in presence of  $0.5 \text{ mol L}^{-1}$  HCl and  $0.05 \text{ mol L}^{-1}$  thiourea, and  $10 \mu\text{g L}^{-1}$  Bi and Hg in presence of  $0.5 \text{ mol L}^{-1}$  HCl and 10% (v/v)  $\text{HNO}_3$ , without thiourea ( $\text{CP} \pm n$ ;  $n = 1, 2, 3$ )<sup>85</sup>

The variation of the analytical signal depending on the number of the pixels of the WIA integration highlighted that over a number of pixels ( $\text{CP} \pm 2$ ) a significant increase of the absorption of the studied elements was not obtained. The sensitivity was at least 3 times higher than the one obtained on a single central pixel of the analytical line. Thus, the calibration curves and analytical performance were evaluated for the WIA signal integrated on the  $\text{CP} \pm 2$  wavelength range.<sup>85</sup> The parameters of the calibration curves and the LOD values for  $\text{CP} \pm 2$  are centralized in Table 2.2.<sup>85</sup>

**Table 2.2.** Parameters of the calibration curves, instrumental and method LODs obtained by CVG–HR–CS QTAAS for 7 days using absorbance measured at peak of transient signal and WIA procedure ( $CP \pm 2$ ) in optimum working conditions<sup>85</sup>

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

<sup>a</sup>The 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; <sup>b</sup>LOD of the method calculated for 0.5 g digested sample, made up to 50 mL and 5 times dilution for measurement; <sup>c</sup>LOQ – limit of quantification considered as  $3.33 \times LOD$ ; <sup>d</sup>Hg – measured without prewashing with Ar of the reaction cell and QTA; <sup>e</sup>As and Bi – measured with 20 s prewashing of the reaction cell and QTA; <sup>f</sup>Sb – measured with 30 s prewashing of the reaction cell and QTA; <sup>g</sup>Se și Te – measured with 20 min N<sub>2</sub> purging of the sample after prereduction and 20 s prewashing of the reaction cell and QTA

The instrumental LOD values ( $\mu\text{g L}^{-1}$ ) 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 the solid samples ( $\text{mg kg}^{-1}$ ) were 0.031 (Hg); 0.016 (As); 0.015 (Bi); 0.008 (Sb); 0.084 (Se) and 0.030 (Te).<sup>85</sup> These values are significantly better than the normal limits permitted in soil for Hg, Se and As. The CVG-HR-CS QTAAS method offered better LODs than the ones obtained by CVG-ICP-OES for Hg, Bi, Sb and Te, but similar for As and weaker for Se.<sup>85</sup> Compared with other techniques, such as FI-HR-CS-HG-QTAAS<sup>82</sup>, HG-ICP-OES<sup>86,87</sup>, HG-STAT-HR-CS-FAAS<sup>88</sup> and CVG-HR-CS ETAAS<sup>57,89</sup>, the method presented better LODs for Hg and As, but weaker in comparison with the HG-ICP-MS method<sup>90-92</sup>. In case of Bi, the LOD value obtained by CVG-HR-CS QTAAS was better in comparison with other methods based on atomic absorption, such as HG-(MM)QTAAS (multi)atomizer QTAAS with hydride generation<sup>93</sup>, hydride generation and detection by dielectric barrier discharge atomic absorption spectrometry (HG-DBD-AAS)<sup>93</sup>, hydride generation and detection by flowing liquid anode atmospheric pressure discharge optical emission spectrometry<sup>94</sup> and HG-ICP-OES.<sup>86</sup> For Se and Te, the LOD values were similar or even better than for the AAS methods<sup>88,93,95</sup>, but weaker than those reported for AFS<sup>96,97</sup> and HG-ICP-OES/MS<sup>86,87,90,91</sup>

#### 2.4. Accuracy of the CVG-HR-CS QTAAS Method

The recoveries for Hg, As and Sb in various food, water sediment and soil CRM samples, obtained by prin CVG-HR-CS QTAAS, are presented in Table 2.3.<sup>85</sup> The recoveries for Se in CRM samples, using different sample treatment procedures for the elimination of the non-spectral interferences of nitrite and  $\text{NO}_x$  and spectral interferences of  $\text{NO}_x$  and  $\text{O}_2$ , are presented in Table 2.4.<sup>85</sup> Based on the recovery in food and environmental CRM samples (Table 2.3.), of  $100 \pm 17\%$  (Hg),  $101 \pm 18\%$  (As) and  $100 \pm 17\%$  (Sb), resulted that the method is not affected by systematic errors, since the extended uncertainty for the recovery includes the value of 100% ( $k = 2$ , 95% uncertainty level,  $n = 3$ ).<sup>85</sup> The  $|z'|$  score values in the range  $0,2-1,1 \leq 2$  indicate satisfactory performance for the CVG-HR-CS QTAAS method and does not generate any signal. In case of Se determination in food and environmental CRM samples, the CVG-HR-CS QTAAS method was prone to a significant negative error (recovery  $63 \pm 23\%$ ,  $k = 2$ , 95% confidence level), when no treatment was applied, for the elimination of the interferences determined by nitrite,  $\text{NO}_x$  and  $\text{O}_2$ . Under these conditions, the majority of the  $|z'|$  values were higher than 3.0, indicating an unsatisfactory performance, which generates an action signal.<sup>85</sup>

**Table 2.3.** Found values for Hg, As and Sb in food and environmental CRM samples obtained by the sequential CVG–HR–CS QTAAS method<sup>85</sup>

CRM	Hg <sup>a</sup>		As <sup>a</sup>		Sb <sup>a</sup>	
	Certified value ±	Found value ±	Certified value ±	Found value ±	Certified value ±	Found value ±
	$U_{\text{CRM}}$	$U_{\text{lab}}$	$U_{\text{CRM}}$	$U_{\text{lab}}$	$U_{\text{CRM}}$	$U_{\text{lab}}$
	(mg kg <sup>-1</sup> ) <sup>b</sup>	(mg kg <sup>-1</sup> ) <sup>c</sup>	(mg kg <sup>-1</sup> ) <sup>b</sup>	(mg kg <sup>-1</sup> ) <sup>c</sup>	(mg kg <sup>-1</sup> ) <sup>b</sup>	(mg kg <sup>-1</sup> ) <sup>c</sup>
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 in soil CRM025–050	99.8 ± 18.0	94.0 ± 22.1	339 ± 20.5	319 ± 40.0	< 3.2	3.2 ± 0.4
Sand CRM048–50G	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 sediment NCS DC78301	0.22 ± 0.04	0.24 ± 0.05	56 ± 10	59 ± 12	–	–
Loamy clay SQ001–30G	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 sediments 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 <sup>d</sup>		0.3–1.1		0.2–1.1		0.8–1.1

<sup>a</sup>Hg determined by external calibration, without prewashing of the reaction cell and QTA QTA; As and Sb determined by external calibration with prewashing of the reaction cell and QTA for 20 s and, respectively 30 s; <sup>b</sup> $U_{\text{CRM}}$  – is the extended uncertainty from the certificate ( $k = 2$ , 95% confidence level), <sup>c</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ , 95% confidence level,  $n = 3$  repeated measurements); <sup>d</sup>|z'| score calculated according to the Eurachem guide<sup>98</sup>



**Table 2.4.** Result for Se determination in CRM by CVG–HR–CS QTAAS with and without various sample treatments and external calibration<sup>85</sup>

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

<sup>a</sup> $U_{\text{CRM}}$  – is the extended uncertainty from the certificate ( $k = 2$ , 95% confidence level), <sup>b</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ , 95% confidence level,  $n = 3$  repeated measurements); <sup>c</sup>Without N<sub>2</sub> purging and addition of 1% (m/v) sulfamic acid after prereduction and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>d</sup>N<sub>2</sub> purging of the samples for 20 min after prereduction and prewashing of the reaction reaction cell and QTA with Ar for 20 s; <sup>e</sup>addition of 1% (m/v) sulfamic acid and N<sub>2</sub> purging of the samples for 10 min after prereduction and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>f</sup>|z'| score calculated according to the Eurachem guide<sup>98</sup>

However, the results are not reliable due to the poor repeatability of the measurements. On the contrary, by purging the solutions with nitrogen, for 20 min after the prereduction in 7 mol L<sup>-1</sup> HCl, or by 1% (m/v) sulfamic acid addition and N<sub>2</sub> purging for 10 min and prewashing of the reaction cell and QTA with Ar for 20 s, the pooled recoveries of 101± 18% and 102± 18% were obtained, which demonstrate the overcoming of the depressive matrix effects in the CVG–HR–CS QTAAS method by the use of any of the two sample treatment procedures. A satisfactory performance was highlighted also by the |z'| values, which were in the 0.1–1.2 range.<sup>85</sup>

The recoveries and |z'| scores for As, Sb and Se (for Se the samples were purged with nitrogen for 20 min) in the SRM® 3280 Multivitamin/Multielement Tablets, also demonstrate the absence of systematic errors and a satisfactory performance, for all 3 elements (Table 2.5.).<sup>85</sup> Work-up of the samples by N<sub>2</sub> purging, for 20 min, was verified for commercially available dietary supplements as well, obtaining a pooled recovery of 102 ± 11% and |z| scores of 0.3–1.9 ≤ 2 (Table 2.6.).<sup>85</sup> The concentrations of As, Sb, Bi and Te in these samples were below the LODs of the CVG–HR–CS QTAAS method, therefore, the results are not presented in the table.<sup>85</sup>

For the food and environmental CRM samples, which had the concentration of elements below LOD, the accuracy of the method was verified in samples fortified with 5 µg L<sup>-1</sup> element. The recoveries and |z'| scores presented in Table 2.7. also demonstrate that supplementary treatment of the samples, with N<sub>2</sub> purging with or without sulfamic acid addition, in case of Te determination, ensured good recoveries and satisfactory performance of the method (|z'| scores 0–1.6 ≤ 2).<sup>85</sup>

A negative systematic error was observed in samples without any pretreatment method, for the overcoming of the interferences of nitrite, NO<sub>x</sub> and O<sub>2</sub> (recovery in the 30 ± 22% range and |z'| scores of 6.7–25.3 > 3). Satisfactory results were obtained in all fortified samples in case of Sb, while in case of Bi in 14 out of 16 samples. In two samples of fish muscle and lobster hepatopancreas, the fortified values for Bi presented negative systematic errors and debatable performance (2.0 < |z = 2.6| < 3.0).<sup>85</sup>

**Table 2.5.** Results obtained for As, Sb and Se concentration in SRM® 3280 Multivitamin/Multielement Tablets by CVG–HR–CS QTAAS using external calibration<sup>85</sup>

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

<sup>a</sup> $U_{\text{CRM}}$  – is the extended uncertainty from the certificate ( $k = 2$ , 95% confidence level), <sup>b</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ , 95% confidence level,  $n = 3$  repeated measurements); <sup>c</sup>N<sub>2</sub> purging of the samples for 20 min after prereduction and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>d</sup>|z'| score calculated according to Eurachem guide<sup>98</sup>

**Table 2.6.** Results obtained for Se determination in dietary supplements by CVG–HR–CS QTAAS method using external calibration<sup>a 85</sup>

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

<sup>a</sup>N<sub>2</sub> purging of the samples for 20 min after prereduction and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>b</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ , 95% confidence level,  $n = 3$  repeated measurements); <sup>c</sup>|z| score calculated according to Eurachem guide<sup>98</sup>

**Table 2.7.** Results for Sb, Bi and Te obtained by the CVG–HR–CS QTAAS method in food and environmental CRM samples fortified with 5 µg L<sup>-1</sup> sulfamic acid<sup>85</sup>

Element		Without treatment <sup>b</sup>	N <sub>2</sub> purging <sup>c</sup>	N <sub>2</sub> purging and sulfamic acid addition <sup>d</sup>
Sb <sup>a</sup>	Found mean concentration ± <i>U</i> <sub>lab</sub> <sup>e</sup> (µg L <sup>-1</sup> )	4.98 ± 0.70	–	–
	Pooled recovery ± <i>U</i> <sub>lab</sub> <sup>e</sup> (%)	100 ± 14	–	–
	z'  score <sup>e</sup>	0.1–1.7		
Bi <sup>a</sup>	Found mean concentration ± <i>U</i> <sub>lab</sub> <sup>e</sup> (µg L <sup>-1</sup> )	4.82 ± 0.72	–	–
	Pooled recovery ± <i>U</i> <sub>lab</sub> <sup>e</sup> (%)	96 ± 15	–	–
	z'  score <sup>e</sup>	0.1–2.6		
Te	Found mean concentration ± <i>U</i> <sub>lab</sub> <sup>e</sup> (µg L <sup>-1</sup> )	1.50 ± 0.33	4.90 ± 0.69	5.34 ± 0.75
	Pooled recovery ± <i>U</i> <sub>lab</sub> <sup>e</sup> (%)	30 ± 22	98 ± 14	107 ± 14
	z'  score <sup>e</sup>	6.7–25.3	0–0.6	0.4–1.6

<sup>a</sup>Sb and Bi determined in presence of 0.05 mol L<sup>-1</sup> thiourea; <sup>b</sup>Te determined without N<sub>2</sub> purging and without 1% (m/v) sulfamic acid addition after prereduction and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>c</sup>Te determined using N<sub>2</sub> purging of the samples for 20 min, after prereduction, and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>d</sup>Te determined using 1% (m/v) sulfamic acid addition and N<sub>2</sub> purging of the sample for 10 min, after prereduction, and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>e</sup>*U*<sub>lab</sub> – is the extended uncertainty in the laboratory (*k* = 2, 95% confidence level, *n* = 3 repeated measurement); <sup>e</sup>|z'| score calculated in accordance with the Eurachem guide.<sup>98</sup>

## 2.5. Precision of the CVG–HR–CS QTAAS Method

The results obtained for Hg, As, Sb, Bi, Se and Te by the CVG–HR–CS QTAAS method in environmental samples, such as sludge from water treatment stations, water sediments and soil, are presented in Table 2.8.<sup>85</sup> The precision based on the extended uncertainty (*k* = 2, 95% confidence level, *n* = 3 repeated measurements), was in the range of 4.6–10.7%. Unfortunately, in several samples, the concentrations were below the limits of detection of the CVG–HR–CS QTAAS method. In case of these samples, the precision was verified by the fortification with 5 µg L<sup>-1</sup> element, obtaining RSD values between 4.4 and 10.5% (Table 2.9).<sup>85</sup> The pooled recoveries for the fortified concentration were in the 98–103% range, with extended uncertainty of ±(11–15)%, while |z| was in the 0.1–1.6 range, indicating a satisfactory performance of the method. For the determination of Se in dietary supplements, using nitrogen purging, the RSD% values were between 4.0–8.6% (Table 2.6).<sup>85</sup>

Regarding the sources of the error, the analysis of aliquots the greatest weight (55–71%), followed by the fitting of the calibration (9–27%) and preparation of the standards and samples (18–21%).<sup>85</sup>

**Table 2.8.** Concentrations of As, Sb, Bi, Hg, Se and Te in real environmental samples determined by the CVG–HR–CS QTAAS method<sup>85</sup>

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

<sup>a</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ , 95% confidence level,  $n = 3$  repeated measurements); <sup>b</sup>Hg determined without prewashing of the reaction cell and QTA with Ar; As and Bi determined with prewashing of the reaction cell and QTA with Ar for 20 s, and Sb with 30 s; <sup>c</sup>Se and Te determined by N<sub>2</sub> purging of the samples for 20 min after prereduction and prewashing of the reaction cell and QTA with Ar for 20 s; <sup>d</sup>The values represent the LOD of the CVG–HR–CS QTAAS method

**Table 2.9.** Results for As, Sb, Bi, Hg, Se and Te obtained by the CVG–HR–CS QTAAS method in environmental samples fortified with 5 µg L<sup>-1</sup> element<sup>85</sup>

	Hg <sup>b</sup>	As <sup>b</sup>	Sb <sup>b</sup>	Bi <sup>b</sup>	Se <sup>c</sup>	Te <sup>c</sup>
	Found value ± $U_{lab}^a$ (µg L <sup>-1</sup> )	Found value ± $U_{lab}^a$ (µg L <sup>-1</sup> )	Found value ± $U_{lab}^a$ (µg L <sup>-1</sup> )	Found value ± $U_{lab}^a$ (µg L <sup>-1</sup> )	Found value ± $U_{lab}^a$ (µg L <sup>-1</sup> )	Found value ± $U_{lab}^a$ (µg L <sup>-1</sup> )
Sludge 1	4.83 ± 0.51	5.08 ± 0.73	5.31 ± 0.67	4.68 ± 0.69	4.78 ± 0.42	4.88 ± 0.59
Sediment 1	4.96 ± 0.51	–	5.41 ± 0.72	4.83 ± 0.70	5.18 ± 0.59	4.85 ± 0.57
Sediment 2	4.80 ± 0.45	–	5.42 ± 0.57	5.17 ± 0.51	5.11 ± 0.77	4.89 ± 0.52
Soil 1	5.02 ± 0.66	–	5.09 ± 0.68	5.09 ± 1.07	5.29 ± 0.68	4.93 ± 0.56
Soil 2	–	–	5.02 ± 0.45	–	–	4.89 ± 0.70
Soil 3	4.76 ± 0.60	–	5.09 ± 0.76	5.22 ± 0.48	5.20 ± 0.65	5.05 ± 0.88
Soil 4	4.83 ± 0.44	–	4.79 ± 0.95	–	5.37 ± 0.56	5.11 ± 0.95
Soil 5	4.75 ± 0.54	–	4.98 ± 0.78	–	5.01 ± 0.52	5.04 ± 0.76
Pooled recovery (%)	98 ± 11	102 ± 14	103 ± 15	100 ± 15	103 ± 12	99 ± 14
RSD (%)	4.6–6.6	7.2	5.3–9.9	4.6–10.5	4.4–7.5	5.3–9.3
z'  score <sup>e</sup>	0.1–0.9	0.2	0.1–1.6	0.2–0.9	0.1–1.3	0.1–0.5

<sup>a</sup> $U_{lab}$  – is the extended uncertainty in the laboratory ( $k = 2$ , 95% confidence level,  $n = 3$  repeated measurements); <sup>b</sup>Hg determined without prewashing of the reaction cell and QTA with Ar; As and Bi determined with prewashing of the reaction cell and QTA with Ar for 20 s, and Sb for 30 s; <sup>c</sup>Se and Te determined by N<sub>2</sub> purging of the samples for 20 min after prereduction and by prewashing of the reaction cell and QTA with Ar for 20 s; <sup>d</sup>the values represent the LOD of the CVG–HR–CS QTAAS method; <sup>e</sup>|z'| score calculated according to the Eurachem guide<sup>98</sup>

## 2.6. Conclusions

The conclusions resulted by the development of the general method for the determination of As, Sb, Bi, Hg, Se and Te are the following:

1. The analytical performance of the sequential multielemental CVG–HR–CS QTAAS method was evaluated for the determination of several CVG elements (As, Sb, Bi, Hg, Se and Te), in various matrices, after microwave assisted digestion in aqua regia and the mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  and classical CVG, using a  $\text{NaBH}_4$  solution in HCl medium;
2. The possibility of the overcoming of the depressive non-spectral interferences was highlighted, originated from nitrite and  $\text{NO}_x$ , on the derivatization of Se and Te to hydride, using sulfamic acid addition and nitrogen purging of the sample, respectively simple nitrogen purging, as alternative to the standard procedure based on sulfamic acid addition only, so that the external calibration could be used, without negative systematic errors;
3. It was highlighted that in case of As, Sb and Bi determination the sample purging with nitrogen or sulfamic acid addition is not necessary, which can be explained by a lower concentration of HCl in the sample, necessary as prereduction medium and derivation to hydrides of As and Sb, respectively the main presence of nitrate, which has a depressive non-spectral interference, insignificant, compared to the nitrite;
4. It was demonstrated that the prewashing of the reaction cell and QTA with Ar for a few seconds (20–30 s), before the introduction of the  $\text{NaBH}_4$  solution, for the determination of As, Sb, Bi, Se and Te, is mandatory for the elimination of the spectral interferences of the  $\text{O}_2$  fine structure background, at low wavelengths of 200 nm and  $\text{NO}_x$  at higher wavelengths than 200 nm, on the spectral lines of As, Sb, Bi, Se and Te, and, therefore, great attention should be granted to this step;
5. Mercury, As, Sb and Bi could be determined using the same CVG conditions, but after prereduction of As(V) and Sb(V) with thiourea;
6. Selenium și Te could be determined only separately from the other elements, due to the different prereduction and CVG derivatization conditions;
7. Mercury was easier to determine, in comparison with other elements, due to the fact that its analytical line was not affected by the spectral interferences originating from  $\text{NO}_x$  și  $\text{O}_2$  and no sample pretreatment, neither prewashing of the reaction cell and QTA was necessary;
8. It was highlighted that a simple nitrogen purging, with or without sulfamic acid addition, after the prereduction step of Se(VI) and Te(VI), was the most appropriate, because it ensured the best sensitivity. It was observed that, by sulfamic acid addition, the necessary

nitrogen purging time can be reduced from 20 min to 10 min, obtaining a similar sensitivity with the one obtained by simple nitrogen purging only;

9. The CVG–HR–CS QTAAS method developed within the PhD thesis has proved to be sensitive, precise, accurate with a simple background correction and applicable on a wide range of samples, with satisfactory performance, regardless of the nature of the matrix and multielemental composition, which allowed the use of external calibration;
10. The developed CVG–HR–CS QTAAS method was characterized by generally better or similar LODs, in comparison with other spectrometric techniques, based on direct sampling from liquid or solid samples by HR–CS GFAAS, ICP–OES and ICP–MS with or without CVG.



## **Chapter 3. The Method with Broad Applicability for the Comprehensive Evaluation of Selected Toxic Element Content of Recyclable (Bio)plastics Based on High-Resolution Continuum Source Quartz Tube/Flame Atomic Absorption Spectrometry**

### **3.1. Situation at International Level. Working Hypotheses and Research Objectives**

The plastic materials are polymers which contain chemical additives, added deliberately for the improvement of their properties.<sup>99–101</sup> The management of recyclable plastic materials is complicated, because the selective collection or subsequent collection is often difficult to be implemented, given the diversity of the plastic materials and their chemical composition. The content of several toxic elements becomes higher in recycled plastic materials than in virgin products.<sup>102</sup> Furthermore, microplastics contribute to the pollution of soil and water by absorption-desorption processes of heavy metals.<sup>102,103–105</sup>

Within the PhD thesis, methods applicable on large scale were developed and validated for the comprehensive determination of As, Sb, Bi and Hg content by CVG–HR–CS QTAAS and Cd, Pb, total Cr, Mn, Ni, Cu, Zn, Sr and Co by HR–CS FAAS in recyclable (bio)polymeric/plastic materials. Bismuth is not regulated in virgin plastic materials and no literature data exists concerning exposure risk but its evaluation is important because of the toxic risks associated with long-term exposure to its inorganic and organic compounds. The methods were validated with regard to limits of detection (LODs) and accuracy (recovery and precision), by the analysis of certified reference materials (CRMs) from PE. In case of Bi, Mn, Ni, Sr and Co, elements which are not certified in CRM samples of PE, the measurement methods were verified by analysis of the samples fortified with elements. The results were statistically interpreted depending on the origin and type of the (bio)polymer.

### **3.2. Materials and Method**

#### **3.2.1. CVG–HR–CS QTAAS and HR–CS FAAS Instrumentation**

The determination of As, Sb, Bi and Hg was conducted with the help of the CVG–HR–CS QTAAS system (Analytik Jena, Jena, Germany), presented in Chapter 2, Section 2.2.1 (Fig. 2.1.). Cadmium, Pb, total Cr, Mn, Ni, Cu, Zn, Sr and Co were determined by HR–CS FAAS using a titanium burner acetylene-air flame mounted in the place of QT.<sup>84</sup> The functioning of the HS55 system in discontinuous mode for the determination of As, Sb, Bi and Hg consisted of the following steps: (i) introduction of an aliquot volume of 5 mL into the reaction cell, which also acts as a gas-

liquid separator, (ii) air purging from the reactor-quartz tube with a  $6 \text{ L h}^{-1}$  Ar flow for 20 s for the elimination of dissolved  $\text{O}_2$ , (iii)  $\text{NaBH}_4$  solution addition, (iv) purging of the generated chemical vapors ( $\text{AsH}_3$ ,  $\text{SbH}_3$ ,  $\text{BiH}_3$ ,  $\text{Hg}$ ) from the reactor, with a  $6 \text{ L h}^{-1}$  Ar flow and introduction in QTA heated at  $950 \pm 10 \text{ }^\circ\text{C}$ , in case of Hg determination, QTA heated at  $150 \pm 10 \text{ }^\circ\text{C}$ . A number of 5 pixels (central pixel  $\pm 2$  pixel) were allocated for the measurement of the analytical line, the other pixels of the spectral line were used for the background correction and peak height measurement was used for all elements. The necessary time for one measurement of As, Sb, Bi was 120 s for each element and 80 s for Hg.

### **3.2.2. Preparation and Analysis of Recyclable (Bio)plastic Material Samples**

Quantities of at most 1 kg of recyclable (bio)plastic materials were collected from various sources, which were washed with ultrapure water and dried. The analytical samples ( $\sim 0.4 \text{ g}$ ) were subjected to HP-MAWD wet digestion in a mixture of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ , using PTFE vessels resistant to pressures of up to 100 atm. Prereduction of As(V) to As(III) and Sb(V) to Sb(III) was conducted according to a similar procedure with the one presented in Chapter 2, Section 2.2.2. The determination was conducted from aliquot volumes of 5 mL test samples or CRMs ( $n = 3$  measurements), by mixing with 2 mL 2.5% (m/v)  $\text{NaBH}_4$  solution stabilized in 0.1% (m/v) NaOH, for the determination of As, Sb and Bi, or 3,5 mL of the same  $\text{NaBH}_4$  solution for the determination of Hg.<sup>84</sup>

### **3.2.3. Validation of the CVG-HR-CS QTAAS and HR-CS FAAS Methods for the Analysis of Recyclable (Bio)plastic Materials**

The CVG-HR-CS QTAAS and HR-CS FAAS methods were validated with regard to LODs and accuracy (recovery with 95% extended uncertainty in an analytical performance study conducted on four PE CRM samples and precision). It was verified if the deviation of the found and certified values ( $\Delta m$ ), represents a systematic error, based on the  $\Delta m < U_{\text{lab}}$  și  $\Delta m < U_{\text{CRM}}$  relations, where  $U_{\text{lab}}$  is the extended uncertainty of the found values in the laboratory and  $U_{\text{CRM}}$  is the extended uncertainty of the certified concentration. The differences from statistical point of view ( $p > 0,05$ ), were evaluated based on the Dunnet's test.<sup>106</sup> The Bi, Mn, Ni, Sr and Co elements, which are not certified in the PE CRM samples, were verified by the analysis of fortified samples. The precision of the methods was evaluated by taking into consideration the combined uncertainty resulted from the individual values of uncertainties, for the preparation of standard solutions and samples, fitting of the calibration curve and analysis of aliquots ( $n = 3$ ). The precision was evaluated based on the uncertainty, while the differences between the samples

were analyzed by the Tukey's test. LODs were evaluated according to the  $3\sigma$  criterion ( $\text{LOD} = 3s_b / m$ ; ( $s_b$ ) – standard deviation of the blank;  $n = 11$ ; ( $m$ ) – slope of the calibration curve).

### 3.3. Results and Discussion

#### 3.3.1. Optimum Working Conditions for the Determination of As, Sb, Bi and Hg by CVG-HR-CS QTAAS and Metals by HR-CS FAAS in (Bio)plastic Materials

The optimum working conditions for CVG-HR-CS QTAAS and HR-CS FAAS are presented in Tables 3.1.–3.3.<sup>84</sup>

**Table 3.1.** Condiții optime de lucru pentru determinarea As, Sb, Bi și Hg în materiale plastice reciclabile și bioplastice utilizând metoda CVG-HR-CS QTAAS în sistem discontinuu<sup>84</sup>

Parameter	Setting			
	Ca	Sb	Bi	Hg
Analytical wavelength (nm)	193.696	217.582	223.061	253.652
Signal measurement	Peak height for all elements			
Number of pixels associated to the analytical line	5 (central pixel $\pm 2$ ) for all elements			
Temperature of the quartz atomizer ( $^{\circ}\text{C}$ )	$950 \pm 10$	$950 \pm 10$	$950 \pm 10$	$150 \pm 10$
Ar flow rate for purging of the reaction cell ( $\text{L h}^{-1}$ )	6 for all elements			
Purging time of the reaction cell before $\text{NaBH}_4$ addition (s)	40	40	40	–
$\text{NaBH}_4$ and $\text{NaOH}$ concentration (% m/v)	2.5% stabilized in 0.1% $\text{NaOH}$ for all elements			
Volume of $\text{NaBH}_4$ solution (mL)/pumping time (s)	2/5	2/5	2/5	2/5
Aliquot sample volume (mL)	5 for all elements			
$\text{HCl}$ concentrat. in sample and standards ( $\text{mol L}^{-1}$ )	0.5 for all elements			
Calibration	External			
Concentration of analytes in standards ( $\mu\text{g L}^{-1}$ )	Multielement solution 0; 0.5; 1; 2; 5; 10			
Number of repeated measurements of standards and samples	$n = 3$ for all elements			

**Table 3.2.** Working conditions for prereduction of As(V) and Sb(V) before chemical vapor generation<sup>84</sup>

Parameter	Element species	
	As(V) and Sb(V)	Hg(II) and Bi(III)
Prereduction reagent	$0.05 \text{ mol L}^{-1}$ thiourea in $0.5 \text{ mol L}^{-1}$ $\text{HCl}$	No
Temperature	$90 \pm 5 \text{ }^{\circ}\text{C}$ in a water bath	–
Prereduction time	30 min for both species	–

The working conditions for the determination of metals by HR-CS FAAS were the ones recommended by the manufacturer and presented in Table 3.3.<sup>84</sup>

**Table 3.3.** Working conditions for the determination of metals by HR-CS FAAS in acetylene-air flame<sup>84</sup>

Element	Wavelength (nm)	Wavelength domain (nm)	Air (L h <sup>-1</sup> )	Acetylene (L h <sup>-1</sup> )	Burner height (mm)
Cd	228.802	0.25	470	50	6
Pb	217.001	0.25	470	65	6
Cr	357.869	0.40	400	100	8
Mn	279.482	0.33	470	80	6
Ni	232.003	0.27	470	55	6
Cu	324.754	0.39	470	50	6
Zn	213.857	0.23	470	50	6
Sr	460.733	0.50	470	65	6
Co	240.725	0.28	470	50	6

### 3.3.2. Performance Study of the CVG-HR-CS QTAAS and HR-CS FAAS Methods for the Analysis of (Bio)plastic Materials

According to Table 3.4., the CVG-HR-CS QTAAS method provides instrumental LODs ( $\mu\text{g L}^{-1}$ ) of 0.033 (As), 0.016 (Sb), 0.039 (Bi) and 0.063 (Hg), and LODs in the polymeric materials ( $\text{mg kg}^{-1}$ ) of 0.010 (As), 0.005 (Sb), 0.012 (Bi) and 0.020 (Hg).<sup>84</sup> Therefore, the method allows the determination of As, Sb, Bi and Hg at concentrations ( $\text{mg kg}^{-1}$ ) higher than 0.034 (As), 0.016 (Sb), 0.040 (Bi) and 0.065 (Hg), considered as LOQs. The limit of detection for As is 100 better than the limit imposed in plastic materials in contact with foods of  $1 \text{ mg kg}^{-1}$ , while the one for Hg is 5000 times better than the one from packaging and packaging waste ( $100 \text{ mg kg}^{-1}$ ).<sup>107,108</sup> However, As and Hg are no longer authorized to be used in plastic materials and objects, intended to come into contact with foods, in compliance with the Regulation no. 2020/1245, the modified and corrected version of (EU) Regulation no. 10/2011.<sup>109</sup> On the other hand, LODs for As, Sb and Hg in the CVG-HR-CS QTAAS method were proved to be 380; 3750 and 375 times lower than the migration limits of 3.8, 45 and  $7,5 \text{ mg kg}^{-1}$  set for plastic materials used in the fabrication of toys.<sup>110</sup>

**Table 3.4.** Characteristics of the calibration curves, LODs and LOQs for As, Sb, Bi and Hg in (bio)plastic materials by the CVG–HR–CS QTAAS method<sup>84</sup>

Element	Calibration curve parameters				LOD		LOQ	
	Intercept (u.a.)	Slope (L µg <sup>-1</sup> )	R <sup>2</sup>	s <sub>b</sub> (a.u.)	(µg L <sup>-1</sup> ) <sup>a</sup>	(mg kg <sup>-1</sup> ) <sup>b</sup>	(µg L <sup>-1</sup> ) <sup>c</sup>	(mg kg <sup>-1</sup> ) <sup>c</sup>
As	0.00450	0.0209	0.9968	0.00023	0.033	0.010	0.109	0.034
Sb	0.00810	0.0470	0.9979	0.00025	0.016	0.005	0.053	0.016
Bi	0.00054	0.0444	0.9957	0.00057	0.039	0.012	0.129	0.040
Hg	0.00360	0.0196	0.9993	0.00041	0.063	0.020	0.208	0.065

<sup>a</sup>Instrumental LODs calculated according to the  $3\sigma$  criterion ( $\text{LOD} = 3s_b/m$ , where  $s_b$  is the standard deviation of the blank signal for  $n = 11$  measurements, and  $m$  is the calibration slope); <sup>b</sup>Limit of detection in (bio)plastic materials calculated for 0.4 g sample mineralized and made up to 50 mL, followed by prereduction in an aliquot volume of 40 mL sample and made up to mL; <sup>c</sup>Limit of quantification ( $\text{LOQ} = 3.3 \times \text{LOD}$ ).

According to Table 3.5., LODs in (bio)plastic materials for the HR–CS FAAS method were (mg kg<sup>-1</sup>): 0.4 (Cd, Cr, Ni and Co), 1.3 (Pb), 0.1 (Mn), 0.2 (Cu), 1.5 (Zn) and 0.9 (Sr).<sup>84</sup>

**Table 3.5.** Characteristics of the calibration curves, LODs and LOQs for metals in (bio)plastic materials by the HR–CS FAAS method<sup>84</sup>

Element	Calibration curve parameters				LOD		LOQ	
	Intercept (u.a.)	Slope (L µg <sup>-1</sup> )	R <sup>2</sup>	s <sub>b</sub> (a.u.)	(µg L <sup>-1</sup> ) <sup>a</sup>	(mg kg <sup>-1</sup> ) <sup>b</sup>	(µg L <sup>-1</sup> ) <sup>c</sup>	(mg kg <sup>-1</sup> ) <sup>c</sup>
Cd	0.0038	0.2588	0.9992	0.00026	3	0.4	10	1.3
Pb	0.0003	0.0367	0.9995	0.00014	10	1.3	33	4.3
Cr	0.0006	0.0550	0.9980	0.00005	3	0.4	10	1.3
Mn	0.0010	0.2316	0.9995	0.00008	1	0.1	3	0.3
Sr	0.0004	0.0302	0.9997	0.00007	7	0.9	23	3.0
Ni	0.0004	0.0657	0.9997	0.00007	3	0.4	10	1.3
Cu	0.0000	0.1517	0.9998	0.00010	2	0.2	7	0.7
Zn	0.0042	0.3385	0.9996	0.00124	11	1.5	36	5.0
Co	0.0005	0.0786	0.9995	0.00008	3	0.4	10	1.3

<sup>a</sup>Instrumental LODs calculated according to the  $3\sigma$  criterion ( $\text{LOD} = 3s_b/m$ , where  $s_b$  is the standard deviation of the blank signal for  $n = 11$  measurements, and  $m$  is the calibration slope); <sup>b</sup>Limit of detection in (bio)plastic materials calculated for 0.4 g sample mineralized and made up to 50 mL; <sup>c</sup>Limit of quantification ( $\text{LOQ} = 3.3 \times \text{LOD}$ )

This means that the HR–CS FAAS method allows the determination of these elements at concentrations higher than (mg kg<sup>-1</sup>): 1.3 (Cd, Cr, Ni and Co), 4.3 (Pb), 0.3 (Mn), 0.7 (Cu), 5.0 (Zn) and 3.0 (Sr). The HR–CS FAAS method is adequate for the determination of Cd, Pb and Cr in

(bio)plastic materials, because the limits of detection are 250–2500 times lower than the RoHS limits specified in the 2002/95/CE Directive<sup>111</sup> and permitted limits in packaging and packaging waste.<sup>108</sup> Also, the method could be considered adequate for the determination of Cr, Pb, Cu and Zn in plastic materials used as packaging for foods and drinks, because LODs are 3 and 2 times lower than the regulated maximum values for Cr and Pb and 25 and 70 times lower, for Cu and Zn, in plastic materials and objects which come into contact with foods.<sup>107</sup> Cadmium, Cr and Pb are no longer authorized to be used in such plastic materials.<sup>109</sup> Also, the HR-CS FAAS method ensures LODs for Mn, Zn and Cu 6, 15 and 25 times lower than the specific migration limits from packagings in contact with foods.<sup>110</sup> However, the HR-CS FAAS method allows the determination of all elements, evaluated in plastic materials used for toys, in accordance with the leachable concentration in 0.07 mol L<sup>-1</sup> HCl solution, indicated in the 2009/48/CE Directive.<sup>110</sup>

The CVG-HR-CS QTAAS method was compared with other methods, which led to the fact that it provides better LODs for As, Sb, Bi and Hg, but especially in case of Sb, because it significantly exceeds the existent analysis methods based on direct solid sampling, such as HR-CS GFAAS, LS GFAAS and EDXRF. Additionally, the CVG-HR-CS QTAAS method presents an extended applicability, being able to analyze a larger spectrum of polymers and biopolymers, in comparison with the reference methods.

### **3.3.3. Accuracy and Precision of the CVG-HR-CS QTAAS and HR-CS FAAS Methods for the Analysis of (Bio)plastic Materials**

According to the data of Tables 3.6. and 3.7., the CVG-HR-CS QTAAS and HR-CS FAAS methods are not affected by systematic errors, because the Dunnett's statistical test provided p values of 0.212–0.750, for the CVG-HR-CS QTAAS method and 0.340–0.816 for the HR-CS FAAS method. Recovery for As, Sb and Hg was in the range of 95–105%, with a relative extended uncertainty of 10–21% ( $k = 2$ ). Recovery of 2 and 5  $\mu\text{g L}^{-1}$  Bi in CRM fortified samples was in the range of 97–106%, with a relative extended uncertainty of 10% ( $k = 2$ )<sup>84</sup>

**Table 3.6.** Accuracy of the CVG–HR–CS QTAAS method for the determination of As, Sb and Hg in polyethylene CRM samples using HP–MAWD in  $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}_2$  mixture<sup>84</sup>

CRM	Certified value $\pm U_{\text{CRM}}$ (mg kg <sup>-1</sup> ) <sup>a</sup>			Found value $\pm U_{\text{lab}}$ (mg kg <sup>-1</sup> ) <sup>b</sup>			Recovery (mean $\pm U_{\text{lab}}$ , %) <sup>b</sup>		
	As	Sb	Hg	As	Sb	Hg	As	Sb	Hg
CE 680k	4.1 $\pm$ 0.5	10.1 $\pm$ 1.6	4.64 $\pm$ 0.20	4.3 $\pm$ 0.9	10.6 $\pm$ 2.0	4.80 $\pm$ 0.90	105 $\pm$ 21	105 $\pm$ 19	103 $\pm$ 19
CE 681k	29.1 $\pm$ 1.8	99 $\pm$ 6	23.7 $\pm$ 0.8	30.7 $\pm$ 4.8	94 $\pm$ 17.2	23.0 $\pm$ 3.8	105 $\pm$ 16	95 $\pm$ 19	97 $\pm$ 17
BCR–680	30.9 $\pm$ 0.7	6.2 <sup>c</sup>	25.3 $\pm$ 1.0	30.3 $\pm$ 3.4	5.9 $\pm$ 0.8	25.5 $\pm$ 2.6	98 $\pm$ 11	95 $\pm$ 14	101 $\pm$ 10
BCR–681	3.93 $\pm$ 0.15	0.82 <sup>c</sup>	4.50 $\pm$ 0.15	3.86 $\pm$ 0.54	0.89 $\pm$ 0.16	4.37 $\pm$ 0.74	98 $\pm$ 14	108 $\pm$ 18	97 $\pm$ 17
Pooled recovery							102 $\pm$ 16	101 $\pm$ 18	100 $\pm$ 16

<sup>a</sup> $U_{\text{CRM}}$  – is the extended uncertainty from the certificate ( $k = 2$ , 95% confidence level), <sup>b</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ ,  $n = 3$  repeated measurements and 95% confidence level), <sup>c</sup>Indicative value

**Table 3.7.** Accuracy of the HR–CS FAAS method for the determination of metals in polyethylene CRM samples using HP–MAWD in  $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}_2$  mixture<sup>84</sup>

Element	CE 680k		CE 681k		BCR–680		BCR–681		Pooled recovery $\pm U_{\text{lab}}$ (%)
	Certified value $\pm U_{\text{CRM}}$ (mg kg <sup>-1</sup> ) <sup>a</sup>	Found value $\pm U_{\text{lab}}$ (mg kg <sup>-1</sup> ) <sup>b</sup>	Certified value $\pm U_{\text{CRM}}$ (mg kg <sup>-1</sup> ) <sup>a</sup>	Found value $\pm U_{\text{lab}}$ (mg kg <sup>-1</sup> ) <sup>b</sup>	Certified value $\pm U_{\text{CRM}}$ (mg kg <sup>-1</sup> ) <sup>a</sup>	Found value $\pm U_{\text{lab}}$ (mg kg <sup>-1</sup> ) <sup>b</sup>	Certified value $\pm U_{\text{CRM}}$ (mg kg <sup>-1</sup> ) <sup>a</sup>	Found value $\pm U_{\text{lab}}$ (mg kg <sup>-1</sup> ) <sup>b</sup>	
Cu	–	–	–	–	119 <sup>c</sup>	122 $\pm$ 13	14 <sup>c</sup>	13 $\pm$ 1	98 $\pm$ 9
Zn	137 $\pm$ 20 <sup>c</sup>	134 $\pm$ 23	1250 $\pm$ 70	1186 $\pm$ 136	–	–	–	–	97 $\pm$ 14
Cd	19.6 $\pm$ 1.4	20.8 $\pm$ 2.5	137 $\pm$ 4	134 $\pm$ 15	140.8 $\pm$ 2.5	138.4 $\pm$ 11.5	21.7 $\pm$ 0.7	22.3 $\pm$ 2.4	101 $\pm$ 11
Cr	20.2 $\pm$ 1.1	19.6 $\pm$ 3.1	100 $\pm$ 5	104 $\pm$ 15	114.6 $\pm$ 2.6	117.0 $\pm$ 11.1	17.7 $\pm$ 0.6	17.2 $\pm$ 2.3	100 $\pm$ 13
Pb	13.6 $\pm$ 0.5	13.3 $\pm$ 1.8	98 $\pm$ 6	93 $\pm$ 10	107.6 $\pm$ 2.8	109.8 $\pm$ 8.9	13.8 $\pm$ 0.7	14.2 $\pm$ 1.8	99 $\pm$ 11

<sup>a</sup> $U_{\text{CRM}}$  – is the extended uncertainty from the certificate ( $k = 2$ , 95% confidence level), <sup>b</sup> $U_{\text{lab}}$  – is the extended uncertainty in the laboratory ( $k = 2$ ,  $n = 3$  repeated measurements and 95% confidence level), <sup>c</sup>Indicative value

The certified concentrations of Cu, Zn, Cd, Cr and Pb in CRM samples (Table 3.7.) were recovered in the 97–101% range (relative extended uncertainty of 9–14%,  $k = 2$ ). The recovery of the 0.2 and 0.5 mg L<sup>-1</sup> Mn, Ni and Co concentrations in fortified CRM samples was of 96–105% (relative extended uncertainty of 7–12%,  $k = 2$ ).<sup>84</sup> The precision of As, Sb, Bi and Hg determination in real samples for the CVG–HR–CS QTAAS method, evaluated from the combined uncertainty ( $k = 2$  and  $n = 3$  repeated measurements), was between 4.1–19.2%. The main contributions of the uncertainty were resulted from aliquots analysis (55%) and fitting of the calibration curves (21%). The precision of metal determination by HR–CS FAAS was between 2.8–9.4%.<sup>84</sup>

### **3.3.4. Element Content According to the Origin and Type of the Recyclable (Bio)plastic Materials**

Fig. 3.1. and 3.2. present the variation of element concentrations depending on the type of the (bio)polymeric materials, regardless of their origin.<sup>84</sup> According to Fig. 3.1., concentration of As ranged from 0.010 mg kg<sup>-1</sup> (LOD) to 0.578 mg kg<sup>-1</sup> and it was over LOD in 58% of the 58 analyzed samples. Concentration of Sb was between 0.005 mg kg<sup>-1</sup> (LOD) and 180 mg kg<sup>-1</sup>, over LOD in 40% of samples, mainly in PET. Concentrations of Bi and Hg were between 0.012 mg kg<sup>-1</sup> (LOD) –3.91 mg kg<sup>-1</sup> and 0.020 mg kg<sup>-1</sup> (LOD) –3.71 mg kg<sup>-1</sup>, with levels over LOD in 85%, respectively 80% of samples. Cadmium, Mn and Sr (Fig. 3.2.) were determined with concentrations in the range of 1.93–14.2 mg kg<sup>-1</sup>, 1.04–15.2 mg kg<sup>-1</sup> and 3.19–157 mg kg<sup>-1</sup>, in 20% from the total of analyzed samples. Copper was determined in about one third of the samples with concentration of 3.24–38700 mg kg<sup>-1</sup>, while Zn in all 58 samples, with concentrations of 1.67–1650 mg kg<sup>-1</sup>. Nickel was determined in only two ER samples, while Pb, Cr and Co were below 1.3, 0.4 and 0.4 mg kg<sup>-1</sup>, in all analyzed samples, matching to the LODs of the HR–CS FAAS method.<sup>84</sup> Although Fig. 3.1. and 3.2. would present at first sight significant variations of element content between the polymeric material types, some observations could be made, with respect to the materials which significantly differ or not, according to Tukey's statistical test.<sup>84</sup> Tukey's statistical test did not indicate significant differences in As content variation between PP, PET and PE based polymeric materials, characterized by the highest As concentrations (Fig 3.1.). Additionally, the statistical analysis showed that the As content was significantly higher in ER, compared to OPE, PVC and PA–PE/PA. In one of the ABS samples, the As concentration was of  $0.578 \pm 0.055$  mg kg<sup>-1</sup>, being close to the maximum values determined in PP, PET and PE. Therefore, the ABS material with high As content, should be considered in the evaluation of As content in the characterization of polymeric materials. Antimony had a significant higher concentration in PET than in PP, RE, PE, PA–PE/PA and OPE. Similarly with As, the Sb concentration from an ABS sample was close to the maximum values found in PP, PE and RE and

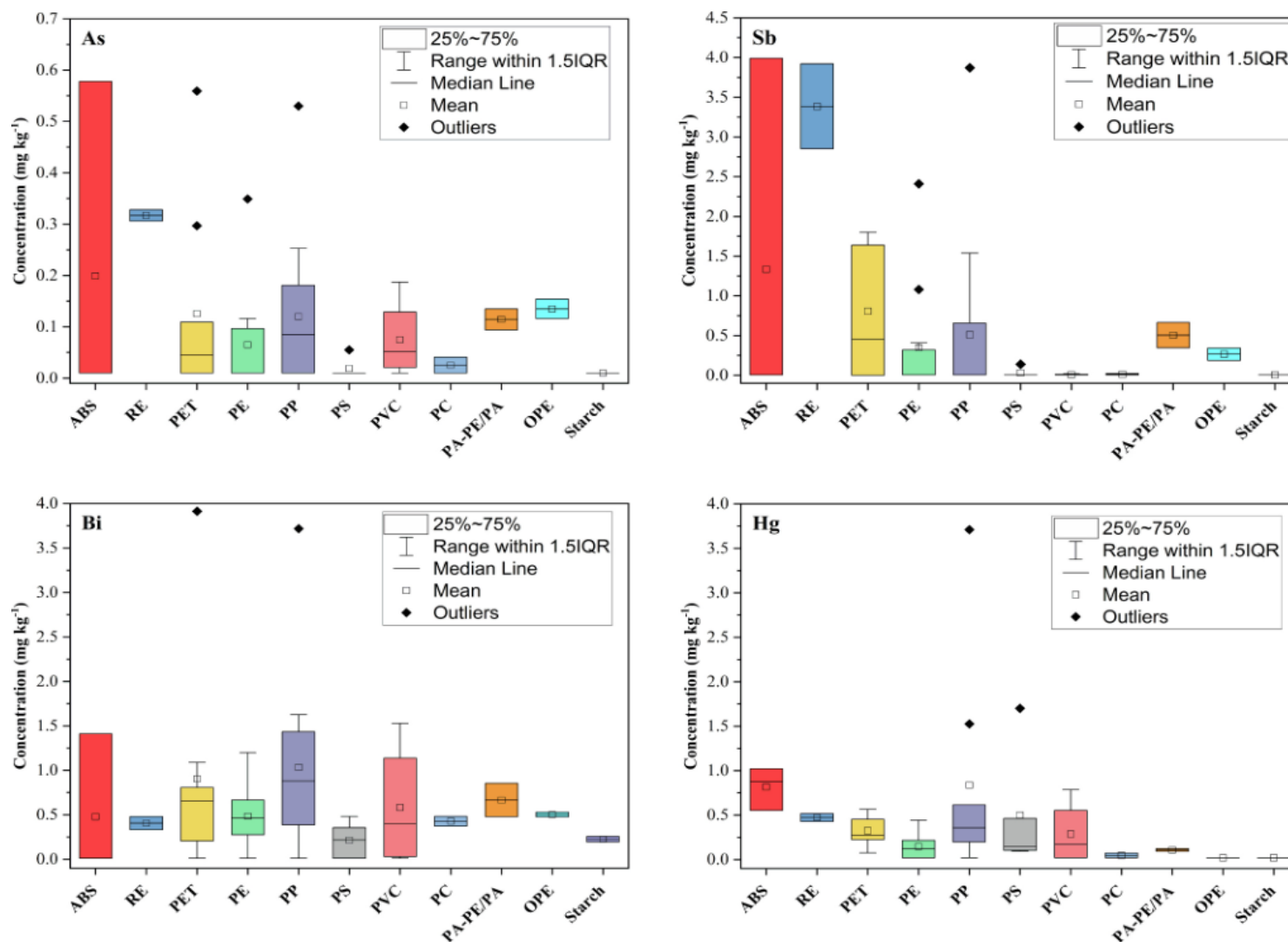


higher than in OPE and PA-PE/PA. Therefore, ABS should also be considered between the polymeric materials with high Sb values. The highest concentrations of Bi were found in PET, PP, PVC, PE and PA-PE/PA, without significant differences for  $p > 0.05$ . However, a significant difference was observed between the higher concentration in OPE than in starch. Similarly with As and Sb, ABS should be included between the polymeric materials with high Bi concentration. With respect to Hg, the polymeric materials with highest concentrations were PP, followed by PVC, ER and PET, but no significant differences were found between these.<sup>84</sup>

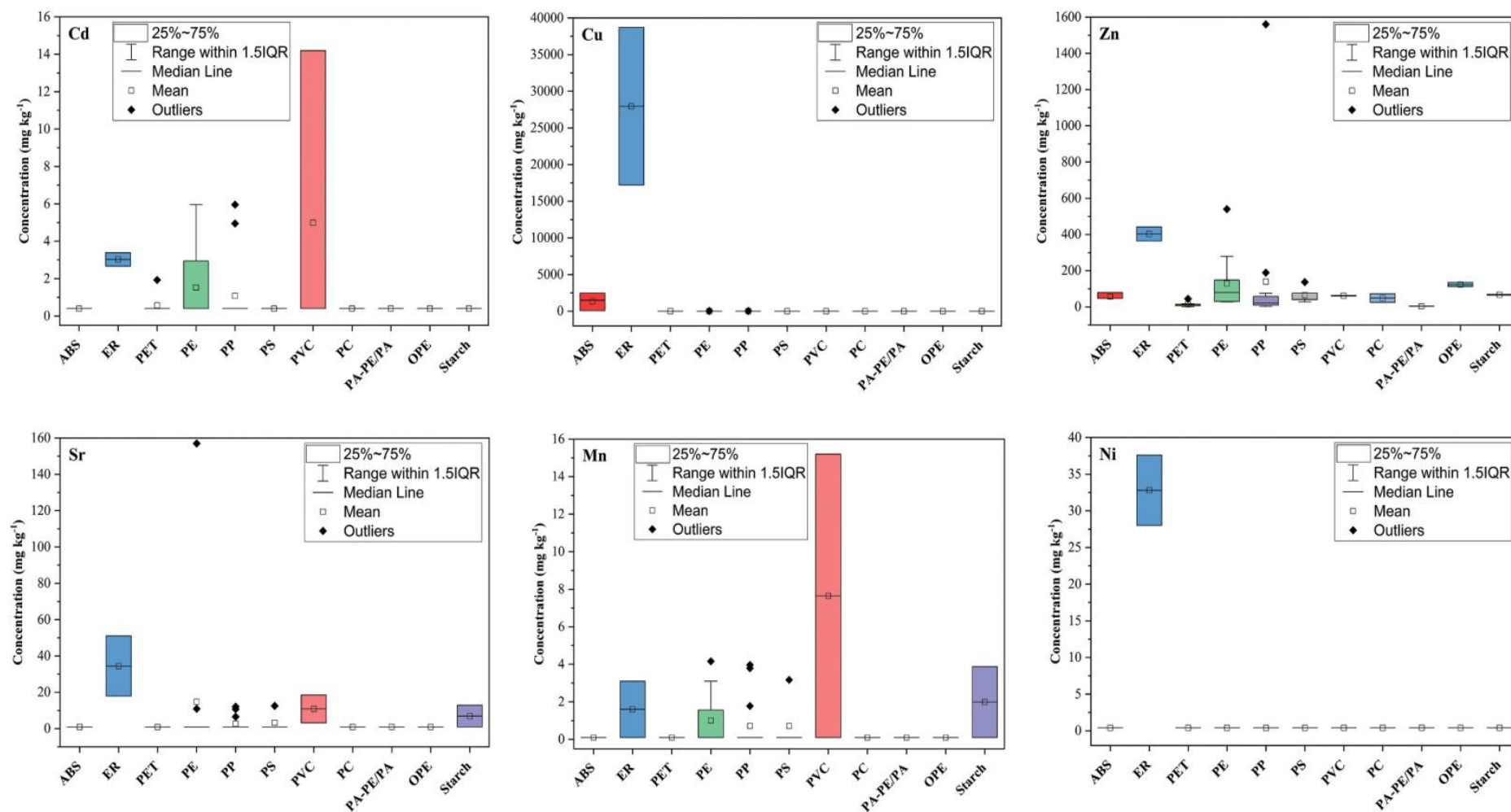
According to Fig. 3.2., the highest concentrations of Cd and Mn were found in PVC and ER, Cu and Ni in ER, but outlier values of Cd, Mn, Zn and Sr can be observed for PP, PE and PS. According to Tukey's test, Cu concentrations from ER significantly differ from those of PP, PE and ABS, while in case of Zn, the content from ER significantly differ from those of all (bio)plastic materials, except PP. Concentrations of Cd and Sr determined over LOD in PP, PE do not differ significantly from those from ER, and Mn in PP compared with PE.<sup>84</sup>

Biopolymeric materials of polymeric hydrides (starch, OPE and PA-PE/PA), had lower concentrations of the elements studied, than synthetic polymers. Zinc was determined in high concentrations in OPE and starch, while Mn and Sr in starch. Yet, Tukey's statistical test did not highlight significant differences. However, the biopolymeric materials or hydrides could be considered as pollution risks, with respect to at least one of the As, Sb, Bi, Zn, Mn and Sr elements. The concentration of Hg in biopolymeric materials and hydrides were below  $0.020 \text{ mg kg}^{-1}$  (LOD).<sup>84</sup>

According to Fig. 3.3., the highest As concentration could be observed in the recyclable materials resulted from WEEE, followed by the ones resulted from medical activities, toys, office supplies, agricultural and domestic activities and food packaging, which presented outlier values. Tukey's statistical test showed that the As content of WEEE differs significantly from the one of recyclable polymeric materials resulted from other sources, such as agricultural, domestic and medical activities, food packaging and construction. It was found that ABS and ER resulted from WEEE and disassembly of IT equipment, have generally the highest As concentrations, followed by medical tools based on PP, PET and PE. The PP polymers resulted from drug packaging and tools and surgical gloves from PE, also presented high As concentrations.<sup>84</sup> Surprisingly, higher concentrations of As were found in polymeric materials in PET-based fruit packagings and PA-PE/PA-based cups, although the use of As compounds in these materials is prohibited in the CE 2020/12450 of the European Commission.<sup>109</sup> Polymeric materials recycled from constructions (PS used as thermal insulator, PC panels for roofs or fences, PVC panelling and PP pipes for drinking water supply and wastewater evacuation) and packaging of cosmetic products based on PE and PET, should be considered as a negligible source of As, because its concentrations were lower than  $0.010 \text{ mg kg}^{-1}$  (LOD).<sup>84</sup>



**Fig. 3.1.** Concentration of As, Sb, Bi and Hg in (bio)polymeric material types, regardless of origin. Antimony concentrations in PET samples were divided with 100<sup>84</sup>

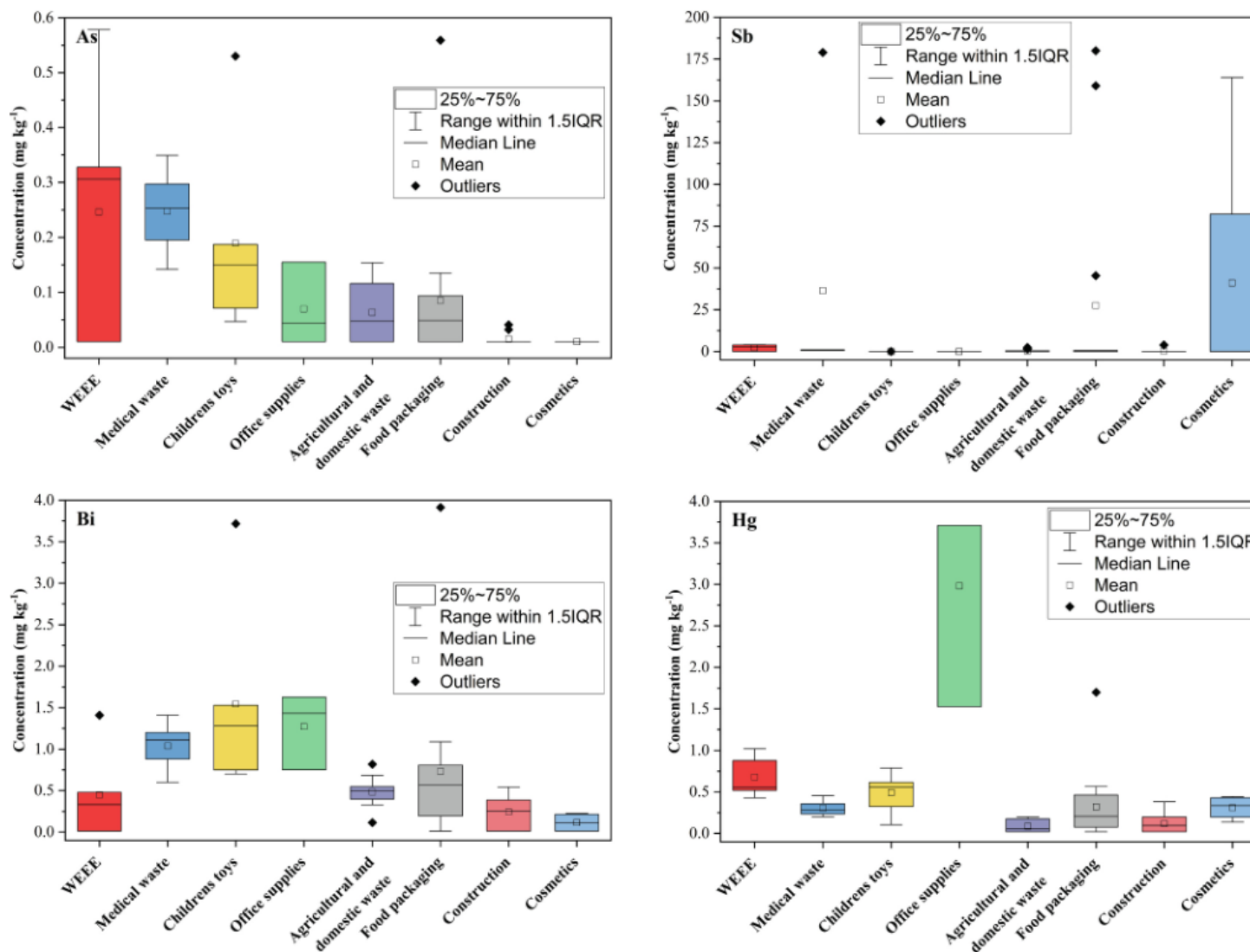


**Fig. 3.2.** Concentration of Cd, Cu, Zn, Sr, Mn and Ni in analyzed (bio)polymeric material types, regardless of origin<sup>84</sup>

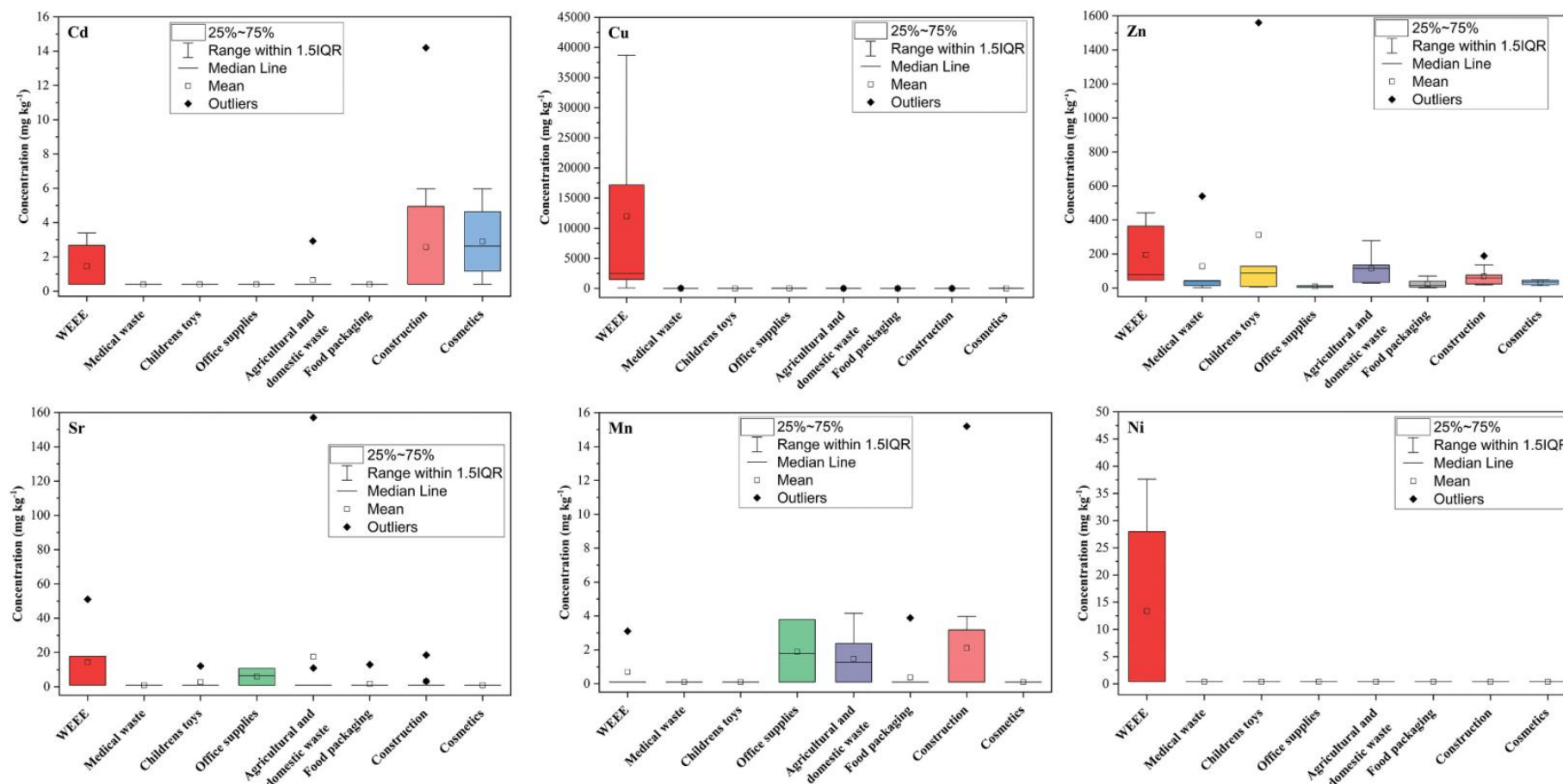
Antimony was characterized by the highest values in recycled materials resulted from food and cosmetic packaging and from those resulted from medical activity. Tukey's statistical test did not indicate significant differences in the variance of Sb content. PS, PP and PVC based materials recycled from constructions and resulted from office activities and toys, usually presented concentrations below the limit of detection of the method ( $0.005 \text{ mg kg}^{-1} \text{ Sb}$ ), similar with Cu, As, with the exception of the black pipe of PP, used for water supply.<sup>110</sup> Bismuth was determined in the majority of materials, regardless of origin, at higher concentrations than  $0.012 \text{ mg kg}^{-1}$  (LOD). The highest Bi values were observed in polymeric materials resulted from toys, followed by food packaging, office supplies and medical activities. Tukey's statistical test did not indicate significant differences in the variance of Bi content, with exception of OPE compared with starch ( $p > 0.05$ ).<sup>84</sup> Generally, Hg was detected in the majority of polymeric materials, regardless of origin, at higher concentration than  $0.020 \text{ mg kg}^{-1}$  (LOD). Concentrations of Hg higher than  $0.5 \text{ mg kg}^{-1}$ , were determined in expanded PS, used for food packaging. Interestingly, the materials of PP-based office supplies also had the highest concentrations of Hg, significantly different from recycled polymeric materials of electronic origin, food packaging, cosmetics, constructions toys and agricultural and domestic activities.<sup>84</sup>

According to Fig. 3.4., Cd was determined in high concentrations in materials resulted from constructions (PVC), cosmetic packaging and WEEE. Copper was found in highest concentrations in WEEE (ER). Concentrations of Zn were generally high in all samples, but especially in WEEE, toys and materials resulted from medical activities, with outlier values. Manganese was determined in higher concentrations in materials resulted from constructions, food packaging, agriculture and domestic and office activities, sometimes with outlier values.

Outlier values of Sr were found in WEEE, materials resulted from agriculture, office supplies, cosmetic products and food packagings and toys. Tukey's test was not suggestive with regards to Cd, Cu, Sr and Mn concentrations, in some of the materials grouped according to their origin, as a result of the too small sample size with concentrations higher than LODs (2 to 4 samples), for which the differences were however significant.<sup>84</sup> Although the concentrations of the determined elements from plastic toys are much lower than the migration limits of  $0.07 \text{ mol L}^{-1} \text{ HCl}$  in solution<sup>109</sup> and lower than those in plastic packagings in contact with foods,<sup>107</sup> a special attention should be granted to the recycling of plastics, because it was demonstrated that the contaminant concentrations might increase by recycling, compared to virgin materials.<sup>100,102</sup>



**Fig. 3.3.** Concentration of As, Sb, Bi and Hg in analyzed (bio)polymeric materials according to their origin, regardless of type<sup>84</sup>



**Fig. 3.4.** Concentration of Cd, Cu, Zn, Sr, Mn and Ni in analyzed (bio)polymeric materials according to their origin, regardless of type<sup>84</sup>

### 3.4. Conclusions

1. The evaluation of the CVG–HR–CS QTAAS and HR–CS FAAS methods was conducted, with wide applicability for the selective determination of metalloids and toxic metals in recyclable (bio)polymeric materials, after HP–MAWD digestion in  $\text{HNO}_3$ – $\text{H}_2\text{SO}_4$  mixture, followed by supplementary oxidation with  $\text{H}_2\text{O}_2$ ;
2. The methods were more sensitive and have better LODs than the direct methods for the analysis of plastic materials, such as EDXRF and LA–ICP–OES/MS, and those based on LS FAAS and ICP–OES, with sample digestion and pneumatic nebulization of the liquid sample;
3. LODs for Mn, Cu, Ni and Zn were better in the HR–CS FAAS method than in ICP–MS and weaker for Cd, Pb and Cr than those from GFAAS;
4. Chemical vapor generation was proved to be essential for obtaining the necessary analytical performance for As, Sb, Bi and Hg determination, in various polymeric materials, at lower concentrations than the regulated maximum values and migration limits indicated in European guides;
5. Arsenic and Sb were detected at concentration levels over the limits of detection of the method in approximately half of the tested materials;
6. Mercury, Bi and Zn were detected in the majority of the polymeric materials, regardless their type, Cu in one third, Cd, Mn and Sr in approximately one fifth of the samples, while Cr, Co and Pb were below LOD in all materials.
7. Tukey's statistical test, conducted on element concentrations in materials with higher values than LOD, showed that, generally, no significant differences existed, with respect to As, Hg and Bi content in recycled polymeric materials. In case of Sb, the test showed that PET-based food and cosmetic packagings had much more higher concentrations than other polymeric materials. Also, higher As, Sb, Bi and Hg concentrations were found in several recyclable polymeric materials based on PP, PE, PS, PVC, ABS and ER, but, in all cases, well below the threshold defined by European guides;
8. The highest concentration of Cu and Zn determined in ER differ significantly, compared to other polymeric materials. Cadmium and Mn were found in the highest concentrations in PVC, Cu, Ni, Sr and Zn in ER. Cadmium and Sr did not differ significantly in PP, PE and ER. In recyclable materials based on biopolymers (OPE, starch and PA–PE/PA hydride materials), at least one of the As, Sb, Bi, Zn, Mn and Sr elements were found above limits of detection;
9. A special attention should be granted to the selective collection and recycling of (bio)polymeric materials, regardless of origin, due to the increased variability of element content observed in this study. On the other hand, in polymeric materials resulted from constructions, based on PS, PP, PVC and PC, the concentrations of the studied elements were lower, mostly below limits of

detection. However, recyclable materials originated from constructions also need special attention because of the considerable quantities of waste resulted from construction sector. The recyclable polymeric materials originated from agricultural and domestic activities (e.g., foils used in agriculture and irrigation tapes), were characterized, generally, by low As, Sb and Hg concentrations, with exception of household garbage bags. Higher concentrations of As, Sb and Hg were determined in OPE bags than in PE bags, in which the content was below the limits of detection of the method. Also, in the PA-PE/PA-based drinking cups, all four elements were above the limits of detection of the method, similar to expanded PS-based food packagings;

10. It was found that WEEE, medical polymeric materials, food and cosmetic packagings, toys and office supplies represent the main sources of As, Sb, Hg, Bi, Cu and Zn after recycling.
11. The results of the study are interesting from the view of open science and citizen science, given the need to recycle and increasing amount of (bio)plastic materials. These could have a negative impact on the environment and human health, although it is considered that added inorganic additives have a reduced mobility in natural environmental conditions.



## Chapter 4. Novelty Elements and Original Contributions of the PhD Thesis.

### General Conclusions

Following the PhD study, high impact scientific results were obtained, within the analytical applications of the CVG–HR–CS QTAAS instrumental technology, for the determination of chemical vapor generating elements, as alternative to the CVG–LR–LS QTAAS classical technology, as follows:

1. A sequential CVG–HR–CS QTAAS method was developed and validated, comprising the most important elements which can be derivatized to chemical vapors (As, Sb, Bi, Hg, Se, Te), being the first in the literature which includes these elements in a single procedure on such an instrumentation;
2. This is the first thesis in Romania, on the instrumental HR–CS AAS concept, produced uniquely in the world by the only manufacturer, namely the Analytik Jena company (Jena, Germany);
3. Following an in-depth study of optimization, both for the prereduction stage of As(V), Sb(V), Se(VI) and Te(VI) and derivatization to chemical vapors, based on the optimum conditions of both stages, it was demonstrated that the elements can be determined in two groups, namely As, Sb, Bi and Hg, respectively Se and Te;
4. The developed method demonstrated more competitive or at least comparable LODs with the ones of other spectrometric techniques used, considering that the determination is optimized for the sequential analysis of the six elements;
5. Three methods were investigated for the elimination of the strongly depressive non-spectral interferences of nitrite and  $\text{NO}_x$ , two strong oxidants resulted in solution following the reaction of concentrated  $\text{HNO}_3$  and HCl, on the derivatization of Se(IV) and Te(IV) to hydrides, demonstrating that a simple  $\text{N}_2$  purging of the sample after the prereduction is much more efficient than the standard literature procedure, based on sulfamic acid addition, because it ensured better sensitivity and LODs. Also, the nitrogen purging – sulfamic acid addition combined procedure reduced the necessary time of the nitrogen purging of the sample, for the elimination of the interferences of nitrite and  $\text{NO}_x$ , from 20 min to 10 min;
6. In case of derivatization of As(III), Sb(III), Bi(III) and Hg(II) to chemical vapors, nitrogen purging of the sample or sulfamic acid addition was not necessary because no depressive non-spectral effects of nitrite and  $\text{NO}_x$  were observed during the derivatization stage;
7. In case of As, Sb, Bi, Se and Te determination, it was demonstrated that the spectral interferences of the background of fine structure of the NO bands above 200 nm and  $\text{O}_2$  below 200 nm, can be eliminated by a simple prepurging of the sample in the reaction cell

and QTA for 20–30 s, before the addition of NaBH<sub>4</sub> solution under alkaline conditions, over the sample in HCl medium. The time of the prepurging has been proved to be very important on the sensitivity of the CVG–HR–CS QTAAS method, being a critical stage. At purging times lower than 20 s, an inappropriate elimination of the spectral interferences over the analytical lines was observed, as well as the very noisy background, and at higher times, the sensitivity of the method was reduced, in case of determination of As, Bi, Se and Te, respectively in a similar way for 30 s in case of Sb. This discovery was based on the fact that the O<sub>2</sub>/H<sub>2</sub> ratio is a critical parameter for the atomization of hydrides and needs to be controlled with attention, being in accordance with the literature data. Supplementary research is needed in this direction;

8. The efficient elimination of the spectral interferences of the molecular bands of NO and O<sub>2</sub> on the spectral lines and background correction by HR–CS AAS technology, has been successfully exploited in the PhD thesis, as a result of the fact that the respective technology allows the spectral background visualization around the spectral line on at least  $\pm 0.1$  nm, simultaneously with the spectral lines, and, therefore, an efficient background correction was obtained, which is not possible in the case of the classical LR–LS AAS technology, in which the measurement is conducted only on the maximum of the spectral line;
9. Usually, the literature data refer to the non-spectral and spectral interferences over the Se line, however, in case of this PhD thesis, the elimination procedures were extended on the Te line, which is a novelty from this point of view, proving that the proposed procedures are efficient for both elements under the same working conditions, which is a particular advantage;
10. The sequential CVG–HR–CS QTAAS method, under optimum conditions, ensured better or similar LODs with other spectral methods, such as CVG–ICP–OES and CVG–LR–TS QTAAS, as a result of the efficient correction methods of the spectral interferences in the PhD thesis, which were completely exploited by the HR–CS AAS technology, respectively by the increase of sensitivity from the increase of the signal by integration depending on the wavelength on the spectral line, possibly offered by the CCD multi-channel detector, compared with the classical technology this line source, which provides measurement only on the maximum of the spectral line, without integration possibility on the spectral line;
11. The very good values of LODs for all chemical vapor generating elements studied (As, Sb, Bi, Hg, Se and Te), allowed the development of some methods unified on various analytical matrices, such as foods, environmental and (bio)polymeric materials, even if a different sequential analysis is necessary for the work-up of the samples, for the elimination of the non-spectral interferences, but the conditions of the elimination of spectral interferences,

only by simple nitrogen purging of the sample from the reaction cell and QTA, were proved to be similar for As, Sb, Bi, Se and Te;

12. The CVG–HR–CS QTAAS method was successfully implemented for the analysis of a significant number of foods of plant and animal origin, environmental samples (soil, water sediments and sludge), respectively recyclable (bio)polymeric materials from various sources, as a consequence of the efficient elimination of the proposed spectral and non-spectral interferences, respectively the outstanding sensitivity and advanced background correction, obtained by sample work-up and HR–CS AAS technology;
13. In case of the analyzed recyclable (bio)polymeric materials, a few differences between the content of some elements were highlighted, according to the nature of the polymer or hybrid material and from the view of recycling source, important aspect in circular economy by selective recycling.

The research directions for the improvement of the CVG–HR–CS QTAAS analytical technology proposed in this PhD thesis would be the following:

1. Implementation of a faster alternative method for the elimination of non-spectral interferences of nitrite and  $\text{NO}_x$ , for the determination of Se and Te, by the decrease of the purging time of the sample with nitrogen, for example by the investigation of an ultrasound-assisted method;
2. The decrease of the reagents' consumption, especially HCl, by using other, more efficient prereduction agents, such as L-cysteine, which operates in much diluted HCl medium, compared to thiourea, at least for As and Sb, respectively a supplementary study in case of Se and Te determination under such conditions;
3. Implementation of some green conditions of derivatization in formic acid, which is a biodegradable reagent, respectively the implementation of *on-line* preconcentration procedures of hydrides on metallic filaments, for the improvement of the method's sensitivity;
4. The technological transfer of the proposed method in routine analysis laboratories on a similar instrumentation or other spectral methods.

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### List of Published Articles in ISI Journals during the PhD Program

No.	Article	Impact factort	Relative influence factor
1	B. D. Szeredai, T. Frentiu, M. Ponta, N. Muntean and E. Covaci High-resolution continuum source quartz tube/flame atomic absorption spectrometry method with broad applicability for the comprehensive assessment of selected toxic elements content in recyclable (bio) plastic materials <i>Spectrochimica Acta Part B: Atomic Spectroscopy</i> , 2024, 218, 106995.	3.2 (Q1) (Place 9)	0.555 (Q2) (Place 3)
2	<b>B. D. Szeredai</b> , T. Frentiu, N. Muntean, A-I. Dudu and E. Covaci 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 <i>Journal of Analytical Atomic Spectrometry</i> , 2025, <a href="https://doi.org/10.1039/D4JA00468J">doi.org/10.1039/D4JA00468J</a>	3.1 (Q1) (Place 8)	0.638 (Q1) (Place 10)

### List of Scientific Communications where Result of the PhD Thesis Were Disseminated

No.	International Conferences	Dissemination mode
1	<b>B. D. Szeredai</b> , T. Frentiu, N. Muntean Multi elemes (As, Bi, Sb, Se, Te, Hg) hidridgeneráláson alapuló meghatározás kidolgozása folytonos fényforrásos atomspektroszkóp segítségével Optimization of chemical vapor generation conditions for multi-elemental determination by high resolution continu-um source atomic absorption spectrometry <i>28th International Conference on Chemistry</i> , 27 – 29.10.2022, Oradea	Oral presentation