



Szent István University

Doctoral School of Environmental Science

Application of element-specific detection techniques and separation methods for determination and fractionation of chemical species of elements in environmental systems

Abstract of the PhD thesis

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The Doctoral School

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1. INTRODUCTION, OBJECTS

The questions concerning the role of chemical elements in agricultural production have been in the interest of agrochemical researches since the middle of the 19th century. The extensive researches in geochemistry, in soil science, in agricultural chemistry and in the different types of physiology gathered substantial amount of research data about the biogeochemical cycling of chemical elements and they developed the methodology to describe these processes better and further improve the efficiency and profitability of crop, vegetable and livestock production.

The industrial revolution of the 20th century along with the urbanization and intensive agricultural production resulted in tremendous changes in the biogeochemical cycles of elements and caused ever increasing pressure on our environment. These facts triggered a great interest to research further the impacts of elements on the environment and on the environmental processes and these research goals raised new requirements in analytical chemical methodology and instrumentation. It was widely recognized that the improvement of the performance of element analysis in this field is not satisfactory with these new scientific goals. These new challenges led to a new research direction in analytical chemistry towards the development of the so called speciation analytical methodology. The speciation analytical method combines separation techniques and structural identification methods with high performance element analytical methods to determine the chemical forms of elements in biological and environmental systems and the biological impact of these identified chemical forms. During the 90's the interest in researching the role of metals and metalloids in the environmental and biological processes exponentially grew, which initiated the development of new scientific nomenclature in this field. The IUPAC recommendations were published in 2000 (Templeton D.M. 2000) with the following definitions:

Chemical species: Specific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure;

Speciation analysis: Analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample;

Element speciation: Distribution of an element amongst defined chemical species in a system;

Fractionation: Process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties (referred to as operational speciation earlier, a simple and relevant alternative for total chemical speciation).

For the above described reasons, the agrochemical and environmental studies require the combination of separation techniques with element analytical methods which are suitable for the detection of both metallic and non-metallic chemical elements. Furthermore, there is a need to elaborate appropriate sampling methodologies and sample separation procedures for speciation and fractionation analytical methods. During my PhD research work I joined Professor György Heltai's two-decade-long ongoing researches of speciation analytical and element fractionation methods and of the development of instruments for such analytical procedures at the Department of Chemistry and Biochemistry, Szent István University. Along with other PhD students involved in this extensive project, I focused on the instrumental development of element specific detection methods by microwave induced plasma (MIP) – optical emission spectrometry (OES). These MIP plasma sources have promising features in this field related to the capabilities of the currently generally used inductively coupled plasma (ICP) optical emission and mass spectrometric (MS) methods. My PhD research project is a continuation of the above mentioned ongoing 20+ years experiment and development of new speciation analytical methods and the improvement of the MIP-OES methodology. Previous PhD candidates working on this project were Józsa 1995; Fekete 2003, Fehér 2009; and Halász 2010. The other area of my PhD studies focused on the methodological improvement of the sequential extraction method that was primarily developed for the fractionation of trace metal content of surface water sediments. I tested the applicability of this method to

examine gravitation dust and biofilm samples and the validation of this extension of use for this analytical method.

Objectives of my PhD work are grouped into two subcategories:

- A.** Extension of application and validation of sequential extraction techniques originally developed for aquatic sediments for analyzing soil, airborne dust particles and biofilm samples. The importance of this research is to obtain a holistic evaluation of heavy metal mobility in the environmental systems expanding the sampling to all sample forms including soil, airborne dust particles, sediment and water.
- B.** Improvement of MIP-OES element-specific detection techniques for speciation analytical purposes for the following three subcategories:
- Coupling the MIP-OES with HPLC systems for elaboration of speciation analytical methods. I was involved in the development of the system by optimization of chromatographic signal generation and signal processing.
 - Testing an improved MIP radiation source with hydraulic high pressure nebulization (HHPN) sample introduction for more robust element specific detection in HPLC.
 - Elaboration of hydride generation MIP-OES method for detecting Hg in water samples. I developed this method through determining the optimal parameters for a signal generation process and I analyzed the practicability of this method for real life scenarios sampling for Hg contamination.

2. MATERIALS AND METHODS

2.1. Samples, sampling techniques and sample preparation for fractionation

Two sampling areas where the monitoring of heavy metal contamination was ongoing for many years were chosen to collect different types of samples for my investigations.

The first area is around the City of Gödöllő and the town of Isaszeg where there is a series of lakes and an ongoing monitoring has been in place since 1995. (Heltai et al. 1998, Fekete et al. 1999, Heltai et al. 2000, Fekete et al. 2003, Heltai et al. 2002, Halász 2010)

The other sampling area is in Slovakia near the city of Kosice where ongoing sampling of industrial and urban airborne dust particles has been taking place for more than four decades. Later sampling sediments from the Hernád River started, too. (Flórián et al. 2003a, Flórián et al. 2003b, Remeteiová et al. 2006, Uhrinová et al. 2005, Matherny et al. 1994, Remeteiová et Rusnak 2006). I joined this ongoing research and started utilizing the sequent extraction method to analyse biofilm samples from the Hernád River.

According to the BCR protocol, the fractionation was developed particularly for testing sediment samples and was validated only for this type of samples. During my research I expanded the use of this method for the following sample types:

- For validation CRM-701 certified sediment reference sample was used (Ure et al 1993).
- Sediment samples were taken from Lake #7 at the City of Gödöllő where former PhD students performed a long-term water quality and sediment contamination monitoring (Halász 2010; Fekete 2003) within the framework of a state funded research grant (www.ragacs.szie.hu), which provided valuable data that my project could use for comparative analysis. All of these data reflect high carbonate, high organic material and significant heavy metal contamination for most samples (Heltai et al. 2000).
- The sediment sampling that is ongoing in Slovakia near the city of Kosice on the Hernád River (Flórián et al. 2003a, Flórián et al. 2003b). Formerly the total element concentration of these samples was analysed by solid probe spectrochemical methods only, fractionation was not performed. I also conducted solid probe analysis to have data comparable to the ongoing testing database, furthermore, I performed fractionation.
- The soil samples came from the town of Nagyhörcsök from the RISSAC Research Group's heavy metal research project administered by Imre Kádár. This project is researching the impacts of heavy metal contamination on plant and animal health (Kádár 1998).
- The airborne dust samples consisting industrial and urban contaminants from the city of Kosice, Slovakia, were collected according to the Bergerhoff method (VDI-Richtlinie 1972) as a part of the ongoing research by Professor Flórián from the Technological University of Kosice, Department of Chemistry. In the previous samples high carbonate, high organic material and also high heavy metal contaminations were detected (Remeteiova et al. 2007).
- The biofilm samples originated from two different locations. The first two samples came from Slovakia near the city of Kosice from the Hernád River, while the other samples came from Hungary from the area of lakes in Gödöllő collected from wood, rock and brick surfaces.

The samples were dried, ground and after that, homogenized. Then the element fractionation was performed by the sequential extraction method according to the BCR protocol (Rauret et al. 2001). To have comparative data, the total element concentrations of the samples were also determined by solids probe spectrochemical method at the Technological University of Kosice. (Horváth et al. 2011)

2.1.1. Fractionation of element content by sequential extraction

The sequential extraction method is an essential way in testing ecotoxicity of heavy metal contamination of sediment and soil samples. This procedure involves the use of extractants such as water, EDTA, HNO₃/H₂O₂, and Aqua Regia (65% HNO₃, 35% HCl). The Community Bureau of

Reference (BCR) recommends the use of the seven step extraction method developed by Tessier et al, 1979. Ure et al, 1993 modified this method and used only three steps and for its validation a certified reference material (BCR-601) was produced, see Figure 1. for details.

This simplified sequent extraction method is less time consuming and it enables the estimation of the mobilizable element contents under different environmental circumstances (Heltai 2005).

BCR three steps Sequential Extraction	Chemical information
Step 1: sample + 0,11 mol dm ⁻³ HOAc	Exchangeable, water and acid-soluble species (e.g. carbonates)
Step 2: Residue from step 1 + 0,1 mol dm ⁻³ NH ₂ OH·HCl (pH = 2)	Reducible species (e.g. Fe/Mn oxides, oxihydroxides)
Step 3: Residue from step 2 + 8,8 mol dm ⁻³ H ₂ O ₂ brake up + 1 mol dm ⁻³ NH ₄ OAc (pH =2)	Oxidisable species (e.g. bound to organic matter or sulfides)
+1 Step: Residue from step 3 + Aqua Regia	Residual fraction
+2 Step: Original sample + Aqua Regia	Pseudo total element content

Figure 1. The EU-BCR recommended three steps extraction method for the element content fractionation of soil and sediment samples

I used the three steps method recommended by BCR for the element content fractionation at the beginning of my project because the ongoing research goes back to 1993 when the original three steps method was utilized. To compare the former test results with my current investigations I used both the original (Ure et al, 1993) and the modified protocol (Rauret et al. 2001) and the modified protocol method. In this way I was able to see the differences between the two methods in the element extraction efficiencies.

The protocol for the BCR sequent extraction method describes the steps for the extraction accurately, the type and quality of the necessary chemicals and their dilution parameters.

2.2. Atom spectroscopic element detection in the extracts

I used the Jobin Yvon 24 inductively coupled plasma – optical emission spectrometer to determine elements from the extracts and solutions. I also utilized the AtomComp 2000 DC arc echelle spectrometer (DCP-OES) for the determination of element concentrations in the solid residual samples at the Kosice Technological University.

2.3. MIP-OES element specific detection techniques and instruments and their improvements:

2.3.1. MIP resonators

2.3.1.1. Beenakker resonator

In the early stage of my research project I used the Beenakker TM010 cavity resonator for plasma generation. This plasma is used as a radiation source for the atomic spectroscopy. The plasma is generated in a quartz discharge tube by high frequency electromagnetic in helium or argon gas. The quartz discharge tube is a Hereaus Suprasil type with the outside diameter of 5 mm and the inside diameter of 3 mm.

For the plasma generation a Helmut Feuerbacher, Ingenieurbüro für Analysetechnik, Tübingen GMW24DR 302 type microwave generator was applied. This generator works at the 2450 ± 20 MHz frequency with magnetron to generate the necessary microwave. The microwave is coupled into the resonator via a KMW 243N type coaxial wave conductor with 50 Ohm impedance. The microwave power can be adjusted between 20 and 300 Watts.

2.3.1.2. Tandem-CMP-MIP-torch

The Beenakker TM-010 resonator was supplemented according to the registered standard of K. Jankowski, A. Ramsza, E. Reszke, Polish Patent Application P-385484 by Edward Reszke (ERTEC ul. Szczecinska 17-21, 54-517 Wroclaw, Poland) with a capacitively coupled microwave plasma resonator (CMP/MIP). See Figure 2. and 3. for details.

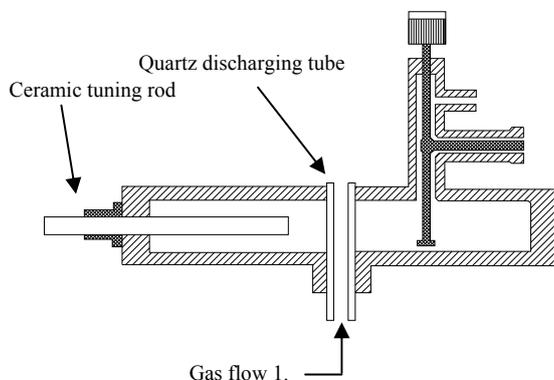


Figure 2. Original Beenakker TM-010 resonator

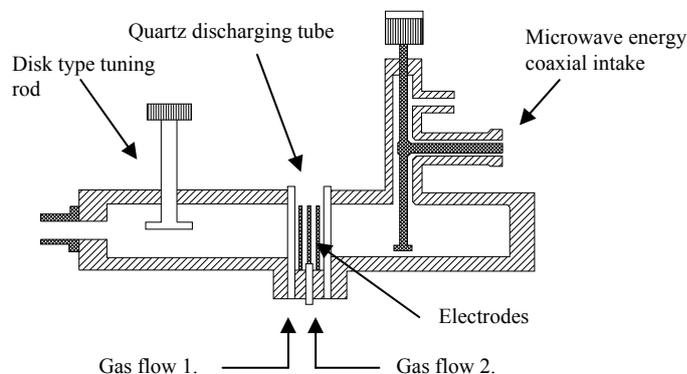


Figure 3. Modified CMP-TM-010 tandem resonator according to Reszke

2.3.1.3. MSP resonator

During my research at professor Broekart (Institut für Anorganische und Angewandte Chemie, Universität Hamburg) I used a low performance small size microwave plasma resonator based on the micro-strip plasma technique (Engel et al. 2000; Bilgic et al. 2000) and I detected the spectrum with a miniaturized CCD-spectrometer. The MSP resonator was built on a copper block that has surface grooves on it to enhance the heat conduction/cooling and serves as an electrode for discharge. A 30 mm x 30 mm sapphire plate is affixed to the copper block with a tiny hole on it ($d=0.64$ mm). There is a copper coating on the surface of the sapphire plate that acts as anti-electrode. The discharge is formed in the small hole at the outlet side of the sapphire plate (Schermer et al. 2003).

2.3.2. Sample introduction into the Beenakker type MIP by hydraulic high pressure nebulization (HHPN)

I used the HHPN by which the impulse type sample introduction can be realized into the MIP discharge. This was necessary due to the limited sample mass flow tolerance of the MIP-discharges (Heltai et al. 1996, Heltai et al. 1999). In this system the continuous carrier eluent (mainly bidistilled water) flow was sustained by a KNAUER made (type-64) HPLC pump. Into this flow a small volume sample solution can be injected by the sampling valve switching the calibrated sample loop into the eluent flow. Because of the very high aerosol generation efficiency, the generated aerosol is desolvated before it is introduced into the MIP. The sample changer valve could be equipped with different size loops (PEEK tubes calibrated to certain volume: 20 μ L, 100 μ L, 455 μ L). Most of the time I used the 20 μ L loop that proved to be optimal in the previous research tests. The size of the necessary sampling loop is determined by the mass flow density through the MIP-discharge. This indirectly influences the absolute detection limits. My experiments shows, if the eluent was pumped with a pressure of 20 MPa and with 1.2 ml/min flow intensity, the sample aerosol reached the plasma in about 1 – 2 seconds.

2.3.3. Hydride generation

I used the electrolysis cell developed by Červený et al. 2007 for the electro-chemical mercury hydride generation (EcMCVG). The two separate cells were manufactured from plexiglas by Rempo Net Manufacturing Co. of the Czech Republic. The cells were 3X3X100 mm in size and

were separated by Nafion®117 (Aldrich, USA) ion exchange membrane. The anode and cathode both were made of 99.999% Platinum (Goodfellow, UK). The surface area of the cathode was 1,200 mm² while the anode was 300 mm². Both electrodes were connected to the laboratory's 0.03 Amperes power supply by copper contacts (DIGI 40, Voltcraft Labornetzgerät, Germany). The anolite solution contained 2M sulfuric acid while the catholite solution was made of 0.05M HCl of the sample and they were pumped by Perimax 12/4 (Spetec, Germany) peristaltic pump through a 0.25 mm diameter Tygon® pipe or a Teflon pipe. Helium gas flow with 4.6 purity value was pumped into the system at three different locations (plasma and electro chemical cell gas flow; gas-liquid separator flow; hydrogen removing cell flow).

2.3.4. Spectrometers

2.3.4.1. Spectrametrics SMI-III

For MIP-OES measurements a SPECTRAMETRICS SMI-III Echelle spectrometer was used in monochromator operation mode.

Dispersion and band width parameters were as follow:

wavelength	dispersion	band width
200nm	0.061 nm/mm	0.0015 nm
400 nm	0.122 nm/mm	0.0030 nm
800 nm	0.244 nm/mm	0.0060 nm

2.3.4.2. Oceans Optics USB2000 – Miniature spectrometer

I used the Oceans Optics USB2000 (USA) miniature spectrometer at the Hamburg University during my laboratory research and this spectrometer was equipped with a high resolution CCD detector (2,048 pixel) (SONY ILX511), which was capable of detecting the 200 – 500 nm spectrum range with a f/4.23 mm focus distance setting.

2.3.5. HPLC-MIP-OES system set up for Cr(III)/Cr(VI)-speciation analysis

The below described detection system was previously developed by the research group directed by my PhD mentor for the Cr (III)/Cr (VI) speciation analysis. I joined this ongoing project at the beginning of my project (Heltai et al 2005, Heltai et Horváth 2006, Heltai et al. 2006, Heltai et al. 2007)

We inserted a C18RP chromatographic column between the sample changer valve and the nebulizer head to add HPLC separation function to the system. Figure 4.

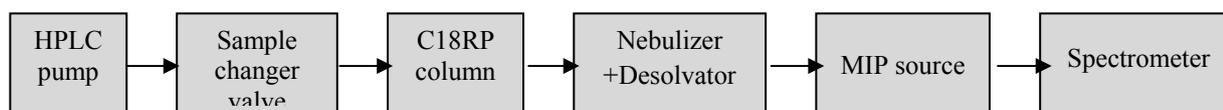


Figure 4. The scheme of the HPLC-MIP-OES detection system

During the experiment we compared the MIP-OES connected to the optimized separation system and the ICP-OES detection systems efficiency. We also compared the differences when using two different types of radiation source and analyzed the interfering matrices and we assessed the calibration problems.

2.3.6. Collection and preparation of water samples for mercury determination

I collected water samples from seven locations around the city of Hamburg, Germany. All the samples were taken from different land use areas to represent all landscape scenarios. Due to the instability of water samples I had to process them immediately in the laboratory. I filtered the samples by using the Filtrak 390 filter instrument and then I divided all the samples into two

separate parts. Half of the samples were analysed directly without adding the analite, while the other half of the samples was analysed by standard addition method using 50 µg/L Hg added to the samples.

Two reference samples were applied for validation the method. One was the SRM NIST 1640 natural water reference sample – although this sample is not labeled for Hg but it is certified for the elements whose interfering effect was evaluated on the mercury determination. This reference sample was used in 10 fold dilution. The other reference sample was the SRM NIST 2781 sewage sludge reference sample with certified mercury content of 3.64 ± 0.25 mg/kg. The sample preparation was done by MARS 5 microwave instrument. The standard addition method with 50 µg/L Hg addition was applied for both reference sample analysis.

3. RESULTS

3.1. Validation of the sequential extraction method for the testing of sediment samples and extending the use of this method for the testing soil, airborne dust particles and biofilm samples

3.1.1. Metodological comparison of application BCR sequential extraction procedure for soil, sediment and airborne dust samples

The sampling areas were selected systematically representing of different heavy metal contaminated situations with different remobilization circumstances.

The major factors causing problems in application of BCR method are:

- 1.) Different organic material composition of the samples of different origin.
- 2.) The batch leaching character of the BCR procedures causing the sample's composition to continuously changing during the process.
- 3.) During the phase separation (centrifugation, decantation) after the leaching steps the readsorption of dissolved analite elements cannot be excluded on the solid surface.

During the validation of sequential extraction method the CRM-701 certified reference sample was processed using the original BCR extraction method to make my data comparable to the previously monitored data done by Heltai et al. 2000, Halász 2010; Fekete 2003 et al. (The sediment monitoring project started in 1995 at the Gödöllő lakes when the modified method was not available.)

The samples coming from different origins have different organic matter and carbonate contents. For example, the gravitation dust samples contain hydrocarbons (oil, PAH) and this causes a not water soluble supernatant phase to appear during the extraction. This partly emulgeated phase was very difficult to separate from the aquaous phase, even increasing the speed and time of the centrifuge would not help much (Heltai et al. 2008; Fekete et al. 2008; Horváth et al. 2009).

The extraction results of the CRM-701 samples for Zn, Cd, Pb and Cu showed statistically acceptable agreement with the certified values, but in the case of several elements significant differences occurred. One reason for the difference is the use of the above mentioned original (unmodified) BCR protocol. The modified protocol requires more accurate acid concentrations in the second and third steps and they changed the hydrogen peroxide's volume in the oxidation step. The second reason for the differences is in the fourth step where the BCR protocol prescripts for the digestion of solid residual Aqua Regia (65% HNO₃, 35% HCl), for this reason I used microwave supported digestion using HNO₃/H₂O₂ mixture (Ure et al. 1993, Rauret et al. 2001).

The airborne dust samples contained high levels of heavy metals that were easily visible just after the first solution step. This fact demonstrated the impact of industrial activity on emission and transportation of heavy metal contamination in urban areas. This has extreme importance in metallurgical industrial areas such as Kosice.

Now, we understand the heavy metal contamination route starting from the airborne dust settling on surfaces, then rain storm washing this to the sewage system and ending up in sewage sludge.

I found a lot lower heavy metal contamination levels of soil samples if the samples were taken far away from the industrial source and according to these findings we have to use the element analytical detection methods with better detection power (e.g. ICP-MS).

3.1.2. Study of re-adsorption phenomena

I paid particular attention to the re-adsorption phenomena during the phase separation by a centrifuge where the dissolved metal ions from the solution get re-adsorbed in the solid phase's surface. This process may cause a systematic error in the results of sequential extraction. I studied the re-adsorption after the third step of the BCR sequential extraction method using the CRM-701 reference sample. The solid residue's upper part and the homogenized solid residue were analysed using the AtomComp 2000 DCP-OES solid probe method (Heltai et al. 2011). All my results detected significantly higher heavy metal concentrations in the upper layer of the solid residue compared to the homogenized solid residue bulk. This confirms the risk of re-adsorption during the sequential extraction methods and it can cause significant errors in case of low concentration samples. The only way we can obtain more reliable estimation of re-adsorption results is that if we could calculate the total balance of dissolved material but in reality this cannot be done.

3.1.3. The comparison of methodological problems connected with sequential extraction of biofilm and sediment samples taken on the same sampling site

These studies were performed to find the correlations between the biofilm and sediment sample composition originating from the same sampling site and to clarify the question how we can apply the BCR procedure on biofilm samples. It was found that the sum of the four-step extraction results of the biofilm samples gave higher concentration results than the direct microwave digestion of the original HNO₃/H₂O₂ samples. The possible reason for this difference is that during the sequential extraction steps the biofilm structures (biopolymers, cells) which retard the release of heavy metals are gradually decomposed so the elements have more chance to get into a solution comparing to the chance they have in the one-step HNO₃/H₂O₂ microwave digestion of sample with original structure.

We repeated the sequential extraction procedures three times and the standard deviations of extraction results were at an acceptable level for reliable statistical evaluation. Other findings showed lower element concentration levels in the first and second step of the fractionation for the biofilm samples compared to the sediment samples. The possible reason for this is the different surface area of different samples and the life cycle of the samples. But in the third step of the fractionation, where the oxidation agents are added and the cells and biopolymer bonds are decomposed, the element concentrations are higher in the biofilm samples. We can also conclude from these findings that the sediment samples have different concentration ratios of organic/inorganic bond elements compared to the biofilm samples.

3.1.4. Comparison of sequential extraction of biofilm samples originating from different support surfaces

We tried to collect biofilm samples from different support surfaces of each region we sampled. We collected two samples from stone surfaces from the Hernad River near the city of Kosice, Slovakia and three samples from stone, brick and wood from the Hungarian Gödöllő-Isaszeg series of lakes. The preparation of the samples started with drying, then grinding to a homogenized phase. The samples then were tested using the BCR protocol with sequential extraction. We utilized the HNO₃/H₂O₂ added. The microwave supported digestion in the HNO₃/H₂O₂ mixture was performed on the original samples and on the solid residual fraction and these samples were analysed with solid probe DCP-OES method in three repetition using the AtomComp 2000 instrument except on samples which were too small in mass (Horváth et al. 2010).

The solid probe analysis results always showed higher element concentrations compared to the sum of four-step extraction results and the pseudo total concentration (original sample direct extraction). The reason could be the sample's heterogenic phase (the very small amount of sample material weighed into the electrode) and the high standard deviation value of OES measurements and with the biofilm samples high silicate content of biofilm samples which cannot be dissolved with

digestion method applied. The summarized extraction results of the four steps in this case were also higher than the pseudo total element concentration and the reason has already been explained above.

Based on the results it can be concluded that during sequential extraction of biofilm samples it is important to determine the optimum ratio between the weight in sample mass and the amount of extractant solution (Heltai et al. 2010; Heltai et al. 2011; Horváth et al. 2011).

There was no significant difference found between the results of biofilm samples element concentration values collected from different support surfaces at the same sampling site.

Comparing the extraction results of the same sample (Kosice biofilm 2) performed with three different sample mass/extractant ratios, it was found that the lower amount of sample intake had higher soluble element concentration. This means that the higher extracting solution volume compared to the sample mass will increase the efficiency of the element extraction from the biofilm samples.

3.2. The improvement of the MIP-OES element specific HPLC detection

3.2.1. Preliminaries: Optimization of a Cr(III)/Cr(VI) speciation analytical method

The development and optimization of a Cr(III)/Cr(VI) speciation analytical method was already an ongoing project when I joined the research group as an MSc student working on my diploma thesis, the research group was led by Professor Heltai György and associates Józsa Tibor és Fehér Balázs. The research group continued the elaboration of hyphenation of HPLC separation with MIP-OES detection system step by step. During the early stage of the research they analyzed the factors influencing the Cr(III) and Cr(VI) species signal generation using the hydraulic high pressure nebulization sample introduction to MIP-OES and ICP-OES. Water was used as eluent and a 20 µL sampling loop proved to be optimal to the MIP source mass flow tolerance. Then they inserted the C18 HPLC column into the system to optimize the eluent methanol concentration using the ion-pair complexing reagent and the chromatograms were evaluated by peak height measurement. Jobin Yvon JY 24 spectrometer was used for the detection of emission signals at the wavelength of Cr 357.8 nm spectral line both for the ICP and MIP radiation sources. Later for the detailed investigations of chromatographic signal formation they used the SPECTROMETRICS SMI-III spectrometer that was equipped with new software developed by Fehér Balázs and this new system enabled them to measure not just the peak height measurement but also the peak area parameters (Heltai et al. 2005; Heltai et Fehér 2006; Heltai et Horváth 2006; Heltai et Józsa 2007; Heltai et Fehér 2007). They tested the effects of the volume of the sample injector loop to the signal formation and based on their experiences they set the optimum parameters for the quantitative measurements.

I joined this work with the calibration of the Cr(III) and Cr(VI) determinations. It was established that the linear dynamic calibration range is two orders of magnitude for both Cr species, but the slope of the calibration lines is different under the chromatographic circumstances both with the ICP and MIP-OES detection. It was also found that the uncertainty of the measurements is lower when peak area was used for the calibration.

The above described research findings provided the evidence that the MIP-OES detection gives species selective response for different Cr species, therefore when it is coupled with HPLC separation, the calibration has to be performed for both species separately. The same consequences were made in the ICP-OES detection system. Altogether based on these facts we can say that during HPLC-plasma emission element specific detection it is not enough to perform only element specific calibration, but species selective calibration is required. We also found that in the MIP-OES system these findings are more relevant and for this reason I started to use and further develop the MIP-torch system that better tolerates solution sample intake.

3.2.2. Elaboration of application of tandem CMP-MIP source as an element specific detector

I started working on the improvement of the MIP-discharge to develop the Cr(III)/Cr(VI) speciation analysis method further in the framework of an international cooperation (Horváth et al. 2009; Horváth et al. 2010; Horvath et al. 2011). The improvement was actually the coupling of the tandem CMP-MIP radiation source with the HHPN sample introduction.

3.2.2.1. Optimization of CMP-MIP gas flows to HHPN sample introduction

During the assembly period of the detection system I had to determine the proper flow rates and the type of plasma gas for the two separate gas inlets entering the torch. The MIP discharge geometry which can be realized by the Beenakker type resonator (toroidal Ar-MIP and diffuse cylindrical He-MIP) was gone through a change in the process, the plasma was ordered around the electrodes and discharge cross-section decreased, but the stability in certain cases improved. For the purpose of using the HHPN sample introduction I evaluated three different arrangements of the gas flow system.

In the first system the two gas inlets to the torch were set up as follows: the vertical gas intake had 25 L/h flow rate of He sample gas and the horizontal gas inlet to the electrodes area had a flow rate of 3 L/h He gas. The incident microwave power was set for 60 W while the reflected power was 28 W. I investigated the system by using different concentration Cu solutions. The sampling loop had 100 μ L volumes and the pure water eluent had a flow rate of 1 ml/min.

In the second system I used the two gas connections to the torch were set up as follows: the vertical gas inlet had 5 L/h flow rate of He sample gas and the horizontal gas inlet to the electrodes area had a flow rate of 20 L/h He gas. The incident microwave power was set for 60 W while the reflected power was 28 W. I investigated the system by using different concentration Cu solutions. The sampling loop had 100 μ L volumes and the pure water eluent had a flow rate of 1 ml/min. In this case the peak heights and peak areas were not comparable and the blank signal was very noisy. The measure's repeatability was limited due to the signal fluctuation. However, the detection limit is lower compared to the other arrangements.

In the third system I used the two gas inlets to the torch were set up as follows: the vertical gas intake had 20 L/h flow rate of He sample gas and the horizontal gas inlet to the electrodes area had a flow rate of 3 L/h He gas. The incident microwave power was set for 60 W while the reflected power was 26 W. I investigated the system by using different concentration Cu solutions. The sampling loop had 100 μ L volumes and the pure water eluent had a flow rate of 1 ml/min. I concluded that this system had a very stable base line and had sharp peaks even with measuring high concentration samples. However, due to the filament formation inclination of the Argon-MIP discharge the system's stability was not sustainable just for a short period of time.

Following these experiments I used only the most stable system for element detection.

3.2.2.2. Calibration

Since the first experimental arrangement showed the best stability I used this system for the quantitative calibration with Cu, Pb and Cd monoelemental solutions in nitric acid. I conducted three repeated parallel measurements.

In case of copper (324.7 nm), the detection limit was 0.24 mg/L and the linear dynamic range can be verified statistically in three orders of magnitude.

In case of lead (368.3 nm), the detection limit was 0.8 mg/L and the linear dynamic range can be verified statistically in two orders of magnitude.

In case of Cadmium (228.8 nm), the detection limit was 1.5 µg/L and the linear dynamic range can be verified statistically in two orders of magnitude.

In case of Cu and Pb, the detection limit values were influenced by the memory effects caused by the electrode material and the deposits on those. The Cd showed lower detection limits due to fact that in this case no contamination by the electrode material occurred. I concluded that in the HPLC detection process we need to avoid measuring high concentration samples to prevent the memory effects caused by the deposits on the electrodes.

The results as of today are very promising for the combination of the HPLC-MIP-OES systems compared to the original parameters of Beenakker resonator. The combined system has one to one and half times wider linear dynamic ranges and the detection limits are comparable. In the near future we need to conduct further research to determine all the interfering factors and the way to eliminate these, especially the deposits caused memory effect problem.

3.3. The development of Mercury (Hg) determination method with the utilization of hydride generation and MSP plasma radiation source

These investigations were performed at the Hamburg University under the guidance of professor J. A. C. Broekaert. In the system development stage my goal was to reduce the dead volume and to reach appropriate fittings for the different gas flows.

To determine the optimal working parameters for the system I was measuring the different influencing factors for the Hg 253.65 nm line intensity and the measurable background intensity near the line.

- 1.) He gas flow rates.
- 2.) The current intensity in the electrolysis cell.
- 3.) The concentration of the catholite solution.
- 4.) The adopting time of the cell.

To find the optimum parameters for the system with the best signal to noise ratio I used 10 µg/L Hg solutions in 0.05 M HCl matrix instead of the cathode solution. The optimum adjusted parameters were as follows:

Sample electrolyte flow rate:	1 ml/min
Catholite solution:	0.05 M HCl
Anolite solution:	2 M H ₂ SO ₄
First gas flow rate:	130 ml/min
Second gas flow rate:	14 ml/min
Third gas flow rate:	20 ml/min
Current intensity of cell:	0.03 A
Power intake into plasma:	40W
Drying medium:	97% H ₂ SO ₄
Software's integration time:	300 msec

3.3.1. Calibration and study of interfering factors

After assembling the optimum parameter system, I calibrated the system in the 0 µg/L to 750 µg/L Hg concentration range both with peak area measure and with peak height measurement with 3 – 3 repeats. I concluded that the system's dynamic range can be verified in order of magnitude, the detection limit was 0.23 µg/L in the case of peak height measurement and 2.51 µg/L for the peak area measurement.

The study of the interfering factors was based on an earlier study in which the interfering factors were enrolled into three groups (Pohl et al. 2008) as follows: 1. interfering hydride forming elements (As, Sb, Se, Te); heavy metals (Cd, Cu, Fe, Ni); and salts (NaCl). These are frequently present in natural water samples as matrix components.

During the investigation of interfering factors I used 50 µg/L Hg (in 0.05 M HCl solution) instead of the catholite solution because at this Hg concentration an appropriate signal generation stability can be achieved and this Hg concentration was easier to wash out from the system, furthermore, it keeps the cell in a continuous active stage. I found strong signal intensity reduction when I added selenium or tellurium to the sample solution, while adding arsenic increased the signal's intensity. I found the similar intensity increase when adding cadmium, copper or antimony to the sample. I also found an intensity increase by adding iron, cobalt and nickel but in this case the relative difference was in the 20% range even with 500 µg/L interfering solution concentration.

Since Na concentration is typically high in natural waters I conducted the Na interference in wider concentration range. I found no change of signal intensity when Na concentrations were low but higher Na concentration rates had a jumping effect on the intensity.

3.3.2. Hg contamination Determination of Hg contamination in real water samples certified reference material samples

I collected seven surface water samples in the proximity of Hamburg, Germany in July 1, 2009. Because of the instability of the water samples I immediately performed the analyses right after filtering. The samples were divided into two parts and I tested the samples in two ways: the half of the samples was analysed directly by external calibration according to the optimal protocol while the other half of the samples was tested following the standard addition method.

According to the tests I concluded that the Hg concentrations in natural water samples fell between 3.9 µg/L and 17.7 µg/L.

I used the ICP-OES [$\lambda(\text{Hg}) = 184,95 \text{ nm}$] determination - including the reference samples too - and the MSP-EcMCVG-OES measuring system to compare the results and to determine the system's applicability and accuracy. The reference samples were divided into two halves as well and tested by both external calibration and the standard addition method.

The SRM NIST 2781 reference sewage sludge sample's Hg concentration was $2.80 \pm 0.59 \text{ mg/kg}$ according to the ICP-OES protocol while it was $2.72 \pm 0.37 \text{ mg/kg}$ by the MSP-EcMCVG-OES protocol. The two separate tests' data are comparable and acceptable equally, but the certified material sample's data was significantly different ($3.64 \pm 0.25 \text{ mg/kg}$). The possible reason for this difference could be that there were analyte losses during in the microwave digestion of the samples or in the filtering process. In the case of the SRM NIST 1640 certified surface water reference sample I did not detect any Hg contamination.

4. NEW SCIENTIFIC RESULTS

4.1. Extension of application and validation of sequential extraction techniques originally developed for aquatic sediments for testing soil, airborne gravitation dust and biofilm samples

I concluded that the environmental mobility of heavy metals in the soil, sediment, airborne gravitation dust and biofilm samples could be evaluated using the sequential extraction techniques. Application of the sequential extraction method based the recommendations of the BCR protocol for different samples require the solving of methodical problems as listed bellow:

- In case of sediment samples when we compare data gained with the original (1993) and modified (2001) BCR protocols, we need to realize that certain elements' (Ni; Cr) solubility rate is different.
- I pointed out that using the BCR extraction protocol during the batch leaching and phase separation operations the phenomenon of re-adsorption occurs and the metal ions already dissolved may get re-adsorbed to the solid phase's surface. This process can cause a systematic error especially in case of determing small analite concentrations.
- In case of solid environmental samples with high apolar organic matter content (e.g. airborne gravitation dust), I found the appearance of a thin oily supernatant phase during the extraction and phase separation operations that can not be separated from the aquaeous phase causing cross contamination between the different fractions.
- Using the BCR fractionation method I found that the mobilizable element content in the different samples have a typical trend, the highest content was found in airborne gravitation dust samples, then in sediments and the lowest concentrations were found in soil samples. This fact gives evidence of that the small amount of airborne gravitation dust plays a role in the transport of industrial/urbanic heavy metal contamination. The reason for the higher heavy metal content of the surface water sediments originates from waste water and surface water runoffs.
- Comparing the heavy metal contamination data of the biofilm and sediment samples originating from different environmental locations and support surfaces I found that the sum of extractable amount of heavy metals in biofilm samples agrees with the sum of extractable amount of heavy metals in sediment samples coming from the same location. The ratio of extracted amounts in different fractions, however, is not the same in biofilm and sediment samples. In biofilm samples I found an insignificant amount of carbonate form and iron and manganese oxide joint fractions, and extractable element concentrations were very high in the fraction bound to organic material related to the sediment samples.
- I concluded that the efficiency of extraction in biofilm samples depends on the ratio of the sample mass/extracting solution, more extracting solution increases the efficiency of the extraction from biofilm samples.

4.2. The improvement of the hyphenated (HPLC)-(MIP-OES) technique for speciation analytical use

During the application of the Cr(III)/Cr(VI) speciation analytical method formerly developed by the research group of my PhD mentor, I found that the circumstances of the HPLC separation strongly influence the performance of the MIP-OES element specific detector, and the same facts can not be neglected when applying the more robust ICP-OES element detection. Based on these facts the species selective calibration is required when using HPLC coupled plasma emission spectrometric element detection methods. These observations mandated to improve the stability of the MIP discharge in the MIP-OES element specific detection method. I utilized the capacitively coupled

plasma – Beenakker cavity resonator tandem MIP torch (developed by Reszke) for these purposes. I optimized the operational parameters of the CMP-MIP discharges in the use of different plasma gases (He; Ar) and for the hydraulic high pressure nebulization sample introduction that enables HPLC connection. I concluded that during the detection of Cu, Pb and Cd from aqueous medium we can achieve 2.5 – 3 order of magnitude linear calibration concentration range applying appropriate and stable discharge forms. The detection limits were between 1.5 µg/L and 0.8 mg/L, but they were also influenced by the memory effects caused by the electrode materials deposits on those.

The above described system can be a competitive alternative in the HPLC-OES element specific detection, but the reduction of interfering and memory effect requires further research.

4.3. Application of the MSP radiation source for the determination of mercury with electrochemical hydride generation

I succeeded in combining the MSP radiation source with the electrochemical hydride generation to efficient mercury (Hg) determination OES method. I determined the optimal operational parameters of the system (gas flow rates, microwave power, flow rates and concentration of solutions used in the system).

I demonstrated that this system has comparable detection limits and the parameters to other analytical detection methods for mercury. This is not only true for the detection limits but also for the linear dynamic concentration range, and based on these facts it is a competitive alternative to other optical emission detection systems. The detection limit was 0.23 µg/L while the linear dynamic range was verifiable in two orders of magnitude.

The study of the interfering factors in this system convinced me that the system is not yet competitive to the traditional chemical hydride generation systems although the matrix effects were not significant for several matrix elements present in moderate concentration levels in water samples. The system was found successfully usable for the detection of Hg from natural water samples.

5. CONCLUSIONS AND RECOMMENDATIONS

I implemented successfully the BCR proposed element fractionation by sequential extraction method for sample types that were not included in the system's existing protocol. I observed that the sum of extractable element fractions are comparable in biofilm and sediments collected on the same sampling site.

I concluded that we need to give particular attention for the re-adsorption phenomenon during the extraction process and we need to acknowledge the fact that the ratio of sample mass/extractant solvent volume also influences the extraction efficiency. These facts suggest that the BCR system needs further improvement, especially in the acceleration speed of the processes and application of continuous flow instead of the batch leaching technique.

The EcMCVG-MSP-OES analytical system I assembled is capable of detecting Hg from environmental water samples even in case of moderate sample matrix level. I determined the optimal operational parameters of this method. The analytical results of real water samples were comparable to the ICP-OES determination results. In the near future, the EcMCVG-MSP-OES analytical system needs further improvement in the reduction of the interfering factors affecting the reliability of element detection.

During the practical use and the research of the usability of the CMP-Beenakker-MIP torch I came to the conclusion that the system is more stable when working with solution samples compared to the previously used original Beenakker type resonator. I optimized the system for the detection of a few heavy metals but the reduction of interfering factors needs further research to improve the usability of the system.

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7. PUBLICATIONS LINKED TO THE THESIS

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1.1. International paper, with impact factor (by WEB OF SCIENCE)

1.1.2. International publishing

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