



SZENT ISTVÁN UNIVERSITY

**Coupling of Plasma emission Spectrometry Methods and
Separation Techniques for Speciation Analysis**

PHD THESIS

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1. Antecedents of the work, aims set

One of the key issues of agricultural and environmental researches is the exploration of the biological role of different chemical elements. Since the middle of the nineteenth century researches have been primarily focused on the elaboration of chemical analytical methods supplementing food production. For several decades, due to the growing environmental load, among the biologists and environment researchers that has gradually appeared that making a map of the biogeochemical cycles of the different elements is inevitable for the creation of such healthy human conditions which are in harmony with our environment. This direction of the research has set new claims for analytical chemistry methods and its devices. Beside the increase of analytical efficiency of the analytical methods, the so-called speciation analytics has also developed.

The linking of separation and structure analytical methods with high-performance element analytical methods, according to the demands of life and environmental sciences, it is possible to answer the question in what chemical forms the different elements appear in our environment and what biological effects the different forms entail. My research is also related to this topic, as I have dealt with development of speciation analytical methods and devices.

In the beginning of my PHD work I joined those who, in my doctoral workplace, had been researching the development of element- and speciation analytical methods based on the development of different plasma radiation sources. These researches are primarily aimed at the utilization of the capabilities and the application possibilities of the MIP (microwave induced plasma) radiation sources and, from time to time they were compared to the possibilities of ICP (inductively coupled plasma). Accordingly, I defined the main objectives of my doctoral work in connection with the development of two speciation analytical methods and a new type of fractionation method:

1. The improvement of the MIP-OES method elaborated for the identification of the ratio of the stable nitrogen isotopes ($^{15}\text{N}/^{14}\text{N}$), according to the claims of the stable ^{15}N -isotopic tracing examinations. Within this scope, I set the aims of applying the CCD detector developed at my PhD department, instead of the previously applied mechanical scanning monochromator; of developing a software necessary to process the transient spectrum signals gained by injection sample introduction technique and of calibrating and validating the method.
2. The improvement, optimization and validation of the method which were developed to Cr(III)/Cr(IV) speciation analysis through the coupling of MIP-OES element specific detector and ion-pair formation HPLC separation. Within this scope, my task was optimization of the high-pressure-hydraulic nebulizer applied for the coupling (fitting the separation and detection system's mass flow); examination of the effects influencing the chromatographic signal-formations; adaptation of the detection method capable of processing the transient chromatographic signal-forming to the available spectrometers and the development of the software necessary for the evaluation.
3. As a result of the software development adapted to the two different speciation analytical tasks, the development of a universally applicable program package appeared, which:
 - a. communicates with the monochromators and the detectors;
 - b. reads and stores the huge mass of data resolved according to the wavelength and time;
 - c. is capable of required processing, evaluation and graphical presentation of the collected data;
 - d. is capable of exporting the evaluated data to accepted data and spreadsheet applications.

4. For the fractionation of the heavy metal pollution of sediments and soils a new type sequential extraction method has been elaborated at my PhD workplace through one after the other application of supercritical CO₂ (SFE), subcritical H₂O, and their combination. I took part in the validation of the new method, comparing the chemical information content of the BCR recommendation and of the SFE method, with the help of certified reference material samples.

2. Materials and methods

2.1. Separation method for the Cr[III]/Cr[VI] speciation analysis

To the HPLC separation I applied the C18 column. The tetrabutyl-ammonium-acetate (*TBAAC*) reagent added to the sample forms ionpair complex with CrO₄²⁻ ions; the Cr³⁺ cation does not enter into any reactions so it passes the column without delay. In the case of methanol elution the Cr-(VI) form goes through the column with significant delay.

2.2. Sample-introduction methods

2.2.1. N₂-gas generation sample introduction from solutions of ammonium-salts to ¹⁵N/¹⁴N speciation analysis

I generated the N₂-gas from solution of ammonium-salts produced by Kjeldahl digestion through oxidation with sodium-hypobromite reagent.

In the equipment schemed by the Fig. 1. the gas-wash-flask filled with NaOBr-solution served as a reaction-vessel; I injected sample solution containing 30-500 µg Nitrogen in it, from which N₂-gas evolved. This was introduced to the atmospheric helium-MIP by the continuously bubbled through carrier-gas Helium through the reaction-vessel. The second gas-wash-flask filled with cc H₂SO₄, placed next to the reaction-vessel, served for the drying of the carrier-gas.

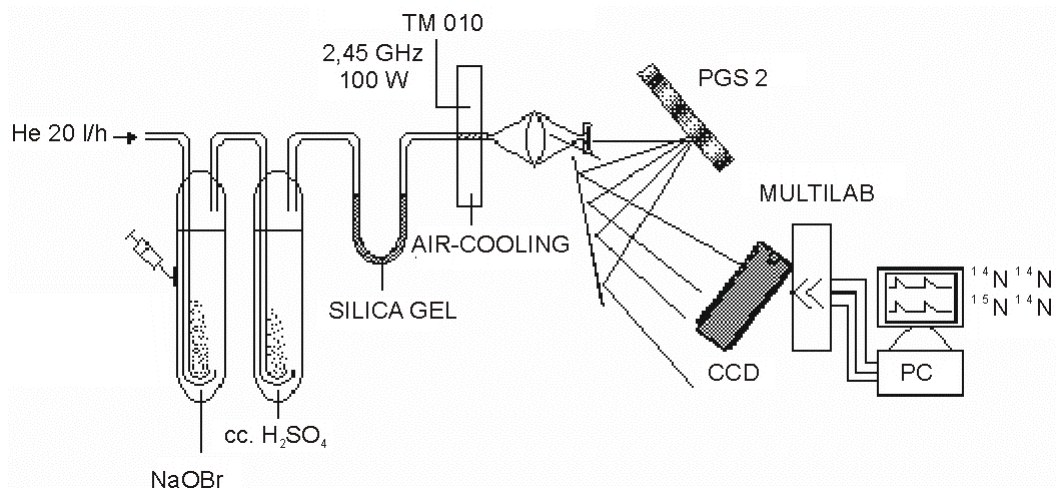


Figure 1. N₂-gas generation sample introduction into atmospheric helium-MIP by oxidation of Ammonium-salt solution

2.2.2. Solution sample-introduction method into MIP, by hydraulic-high-pressure nebulization for Cr[III]/Cr[VI] speciation analysis

The highly efficient hydraulic-high-pressure nebulizer (HHPN) can be directly applicable for HPLC coupling. When high-pressure (100-200 bar) liquid is pressed through the 10-30 µm diameter nozzle the emergent liquid filament collides on the impact bed at a suitable distance (2-4 cm), then fine size distribution aerosol is formed, which is transported by the plasma sustaining He gas flow in the spray chamber, which contains the impact bed.

The high-pressure liquid flow necessary for nebulization can be produced with the help of the HPLC pump, as the HHPN-head is directly connected to the HPLC-column. In the case of $1 \text{ cm}^3 \cdot \text{min}^{-1}$ liquid flow and 50% nebulization efficiency, HHPN could be fit to the massflow-load tolerance capacity of MIP with a desolvation unit. In the desolvation unit, demonstrated the Fig. 2., I used radiative heating, and then I removed water vapour from the system by water-cooling.

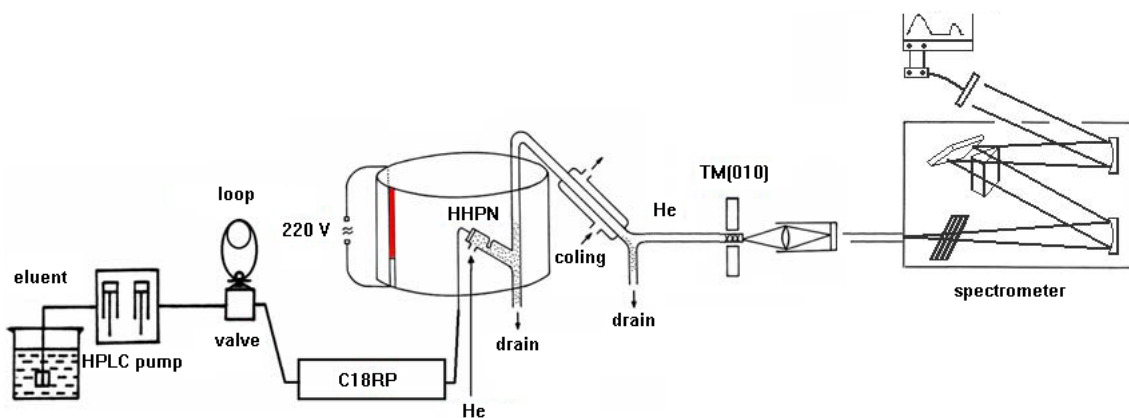


Figure 2.: The system applied for Cr speciation analysis

2.3. The emission radiation source applied: microwave induced plasma

2.3.1. Generator

I used GMW24DR 302 type microwave generator operating on 2450 ± 20 MHz frequency, up to 300 w power.

2.3.2. Resonator

During my experimental work I used a TM (010) mode brass cylindric resonator cavity of 88 mm internal diameter and of 15 mm internal cylinder height, and of water- and pneumatic air-cooling.

2.3.3. Torch

I applied a Quartz discharge tube of Hereaus Suprasil, of 5 mm external, 3 mm internal diameter.

2.4. Spectrometers

2.4.1. PGS-2 grating spectrograph equipped with CCD-detector to determination of $^{15}\text{N}/^{14}\text{N}$ isotopic ratio

To wavelength resolution of MIP-emission I used a PGS-2 type spectrograph. In the focal plane I replaced the photo plate with a CCD detector containing 2592 photodiodes, which was originally produced to bar code reading equipment. The detector is capable to simultaneous recording of 10 nm wide wavelength window in the range above 300 nm wavelength.

There is a significant wavelength shift of the rotation-vibration band head lines corresponding to the given vibration transition of the N_2 molecules with different isotopic composition ($^{14}\text{N}^{14}\text{N}$, $^{15}\text{N}^{14}\text{N}$, $^{15}\text{N}^{15}\text{N}$), so they each can be detected by scanning some nm wide window, and from the measured intensity ratio after proper calibration the $^{15}\text{N}/^{14}\text{N}$ isotope ratio can be determined.

I processed the signals of the CCD detector by a computer. Reading the pixels is a process where they come one after the other, and the duration of reading all pixels determines the perceptible shortest duration of integration (8 s). I developed an own program to evaluate two-dimensional matrix of data formed in the case of measuring transient signals in the function of time and wavelength.

2.4.2. Applying of Spectrametrics SMI-III Y-plazma-spectrometer to MIP-radiation sources, for Cr[III]/Cr[VI] speciation analysis

In the course of Cr speciation I applied a high-resolution echelle-spectrometer built together with a DC Y-archplasma-radiation source; through replacing the original Y-plasma by the microwave plasma resonator used by me.

The original software belonging to the spectrometer did not allow the receiving and the processing of transient signals, so I developed a new program for that; it is run by a computer attached to the spectrometer through an RS-232 serial port.

2.5. Data recording and data processing softwares

In the course of my research work I had to face with the problem that though the carrying out of such tasks required the recording and processing of huge mass of data, there was no software available for me which could support the tasks properly. One of the reasons of the problem was that the hardware used by us was a very old construction (Spectrametrics spectrometer) and the special software developed to the device had originally been developed for the computers having been in service for 25 years. The other problem derived from the fact that the original softwares supported only the routine analytical processes and were not applicable for the method development aimed by me. Therefore, I developed my own software to support my tasks; I reviewed its most important parameters among the results of my work.

2.6. Validation of H₂O/CO₂ sequential extraction (SFE)

I took part in the validation of the fractionation method elaborated by Heltai et al (2000). My intention was to compare the chemical information contents gained according to the EU-BCR recommendation and by the SFE method, as it is demonstrated in the following table:

3 STEP SEQUENTIAL EXTRACTION SCHEME OF BCR	Chemical information
0,11 mol l ⁻¹ HOAc	Exchangeable, water and acid-soluble species (e.g. carbonates)
0.10 mol l ⁻¹ NH ₂ OH.HCl at pH=2	Reducible species (e.g. Fe/Mn oxides, oxihydroxides)
8.8 mol l ⁻¹ H ₂ O ₂ followed by 1 mol l ⁻¹ NH ₄ OAc at pH=2	Oxidisable species (e.g. bound to organic matter or sulfides)

SFE SEQUENTIAL EXTRACTION	Chemical information
Supercritical CO ₂ (in SFE)	CO ₂ – soluble mobile organic fraction
Subcritical H ₂ O (in SFE)	Water soluble fraction
H ₂ O(95%)/CO ₂ (5%) (in SFE)	carbonate bound fraction

2.6.1. Elemental analysis

From each fraction I determined the concentration of 6 elements (Zn, Cd, Pb, Ni, Cr és Cu) by a Jobin Yvon 24 type ICP optical emission spectrometer.

3. Results and discussion in the case of the nitrogen isotopic ratio measurement

3.1.1. Correction of the drift of plasma in the course of time

I controlled the change of the measuring system in the function of time (drift) by periodically repeated measurement of a chosen control sample (500 µg total-N and 3,6 ¹⁵N at % content). To the measured values I fitted a polynome of the second degree on the basis of the sequential number of the measurement and I corrected all measurement results by this polynome.

3.1.2. Determination of the change of $^{15}\text{N}^{14}\text{N}$ band head intensity

Intensity measurement of the $^{15}\text{N}^{14}\text{N}$ molecule bandheads was made difficult by the fact that rotation-vibration spectrum lines appeared from the interfering molecules (OH; CO) present in the plasma on the detected wavelength range. The $^{15}\text{N}^{14}\text{N}$ bandhead was overlapped by a line of these interfering molecules. To eliminate that, I elaborated an interfering band-system-line-correction valid to the given circumstances based on the intensity ratio of the interfering line-system.

3.2. Calibration of the N15/N14 isotopic ratio determination

The net intensity of the molecular bandheads of different isotopic composition increased monotonously in the function of the injected N-quantity, but in the case of a given mass of nitrogen the intensity of the bandheads depended also on the isotopic concentration.

Intensity ratio of the two bandheads (H) detected proved constant in a given mass range and this allowed the calibration of the isotopic ratio determination.

$$H = \frac{A(^{15}\text{N}^{14}\text{N})}{A(^{14}\text{N}^{14}\text{N})}$$

A = integrated area of the change in the function of time of net bandhead intensities measured in the case of samples of different isotopic composition. The H ratio changed in proportional to ^{15}N at% of the samples. On the measured points a linear calibration curve can be fit ($R = 0,9991$); the isotopic ratio determination relative standard deviation calculated from the residual standard deviation in the middle of the measuring range is $s_c/c = 3,75\%$.

4. The results and discussion in the case of the Cr[III]/Cr[VI] speciation analysis

4.1. The effect of the volume of the sampling loop on the signal formation

Into water eluent, using sampling loops of different volume (455 μl , 100 μl , 20 μl), I injected solutions containing Cr(VI) of the same quantity (500 ng) and of the same concentration (5 ng/ μl). I found out that in the case of peak-height measurement, it is the most favourable to apply the smallest loop size (20 μl). However, when peak area was determined I received the maximum signal in the case of 100 μl loop size, with the minimum standard deviation. Taking into consideration also these experiments, I carried out the quantitative measurements in most of the cases with 20 μl sampling loop, which allowed the evaluation on the basis of both the detection of the peak-height and the peak area determination with acceptable precision and accuracy.

4.2. The effect of the chemical form of Chromium (Cr^{3+} illethe CrO_4^{2-}) on the signal formation in aqueous medium

Using the HHPN-MIP-OES system in aqueous medium, by measuring a 20 μl solution containing Cr(III) and Cr(VI), on the basis of calibration lines gained by peak-height measurement I stated that the CrO_4^{2-} anion-form gives smaller signal than the Cr^{3+} cation-form. In the case of the given sample-introduction method evaporation and atomization rate of the aerosol containing two different chemical forms are of different degrees, and in the case of transient signal formation it causes significant differences. The different signal formation of the two forms cannot be eliminated even by an evaluation based on the peak area determination. In the case of signal integration the linear dynamic range of HHPN-MIP-OES covered three orders of magnitude regarding both chromium forms, and the detection limits were of 1-5 ng order of magnitude.

4.3. The effect of the eluent's metanol content on the signal formation

According to my experiences the rise of metanol concentration tunes out the MIP discharge and the stability can be restored only by the retune of the cavity. Accordingly, the effect of the organic

solvent vapour on the background radiation (blind value) intensity cannot be followed directly. I observed that the signal decreasing effect of the methanol vapour was strongly dependent on the loop size and on the chromium ionform as well. In the case of smaller loop sizes (20 μl and 100 μl), the Cr(VI) signals decrease in much higher degree under the effect of methanol than the Cr(III) signals. On the basis of this investigation, those limits can be set between 15-20% (V/V) where the methanol content of the eluent does not generate further Cr-signal decrease.

I established that from the point of view of the separation, the minimal 15% (V/V) methanol content could be considered optimal. In the case of 20% (V/V) methanol content the separation of Cr(III) and Cr(VI) is no more complete, while in the case of 10% (V/V) methanol content the dissolution of Cr(VI) drags on too much, the signal were widened and tailed.

4.4. The effect of the organic complex reagent (TBA-Ac) on the signal formation

I studied the effect of TBA-Ac applied in $3 \cdot 10^{-4}$ mol dm^{-3} concentration on the signal formation, in HHPN-MIP-OES system in the case of samples containing Cr(III) and Cr(VI), applying distilled water eluent. In the case of Cr(VI) I observed signal decline, which could be explained by the higher energy demand of the evaporation and atomisation of the ionpair complex.

4.5. The recovery of the TBA-Cr(VI) ionpair complex from the C-18 HPLC column

I found out that in experimental circumstances the recovery of the Cr(VI)-TBA complex from the column approximates the 100%. At the same time, it was also observed and verified, that in the case of the complete configuration of the HPLC-HHPN-MIP-OES system and the presence of all reagents (TBA-Ac, methanol etc.), the peak-height and the peak area of the signals formed under the effect of injection Cr(VI)-solution containing the same quantity of Cr were significantly smaller than the value gained in the case of injection of Cr(III).

This difference is due to the effects impeding the evaporation and the atomisation of Cr(VI) and not to the incomplete recovery of Cr(VI), as it was experienced in the case of the aqueous solutions, too.

Compared this to the previous experiments (Heltai et. al., 1999), it can be established that in the case of MIP-OES detection, in aqueous medium, with peak area detection, the difference between the Cr[III]/Cr[VI] peaks declines compared to the evaluation according to peak-height. This difference decreases also in the case of applying the separation system compared to the previously applied evaluation method, but the difference remains significant in both cases. On the basis of this it can be established that the detector gives species selective answer.

5. Data collection, data processing software package

I applied the software package in the course of the above presented research work. I carried out the recording and the evaluation of the measurement with the software package.

I wrote certain components of the program package in Turbo Pascal, Pascal for Windows and Delphi languages.

5.1. Spectrametrics data collection software

The software made for the Spectrametrics system is completely able to take advantage of the capabilities of the detector, supports the measurement adjustment and in the course of the measurement process it continuously provides the user with information on the measurement process and on the accuracy of any adjustments.

5.2. Data evaluation software

I developed the software in Turbo Pascal for Windows surroundings. It is able to read the data collected by the data collection softwares; to reproduce graphically the two-dimensional matrix of data according to course of time or wavelength; to manage those data; to compare the data series

according to course of time of the parallel wavelength ranges allowing this way the filtering of the interfering lines and the carrying out of the background correction; to smooth the measured data; to restrict automatically the transient signals and the chromatographic peaks, and on the basis of the previously mentioned to determine the peak area.

6. The result of the comparison of fractionation methods

According to my achievements, the results of the sequential extraction steps carrying similar chemical information are comparable in the case of Ni, Cr and Cu (BCR 1. step / sum of (H₂O/CO₂) 2. and 3. steps). In the case of Zn, Cd and Pb huge difference arised between the two methods. This derives from the fact that the extraction time applied in SFE system did not prove sufficient to dissolve the carbonates. In the course of later researches this problem was eliminated by increasing the extraction time to 90-180 minutes.

However, the information content of the SFE process is different from the BCR-process. Regarding acetic acid dissolution according to BCR recommendation, the sum up of only one fraction characterises the mobile element fraction. The SFE method divides this into two fractions (water-soluble fraction and fraction bound in carbonates). One significant comparative advantage of the SFE process that it is much less time-consuming than the BCR method. Besides, in aqueous and CO₂-soluble extracts it is possible to search and identify species in their original chemical state. The aqueous extracts are usable to test ecotoxicological effects of sediments polluted with heavy metals.

7. New scientific results

1. I developed a speciation analytical method to determine the ratio of stable Nitrogen isotopes (¹⁵N/¹⁴N) by MIP-OES system based gas-generation sample introduction, with CCD-spectrum detection which was applied for plane-grating monochromator, and that helped me to succeed the correction of the other molecular emission overlapping of the emission of N₂. The precision and accuracy of the method proved suitable for the evaluation of stable ¹⁵N tracing in agrochemical experiments.
2. I developed a chromatographic signal processing method for the Cr[III]/Cr[VI] speciation analytical method, which is based on HPLC separation and carried out with MIP-OES detector and a hydraulic-high-pressure-nebulizer, and I also evaluated the effects influencing the chromatographic signal formation. I established that in the case of chromatographic evaluation based on peak-height measurement, the application of the smallest, 20 µl injection loop size, while in the case of evaluation based on peak area determination, the application of 100 µl loop size is the most favourable. The methanol content of the eluent should be set between 15-20% (V/V), taking into consideration the loadability of the detector and the optimum of the chromatographic separation. The developed method is applicable with species selective calibration for analysis of water samples in 50-5000 ng/ml Cr concentration ranges with 80-130 ng/ml detection limit.
3. I developed a software package for the above mentioned two speciation analytical tasks; it communicates adequately with the Spectrametrics spectrometer, which applies echelle grating wavelength resolution and it is usable both in one- and multichannel modes, and through a suitable interface card with the PGS-2 plane-grating spectrograph equipped with CCD detector. The program adequately reads, stores, processes and evaluates the measured data either according to wavelength or course of time; in the course of the measurement process it ensures suitable user surface for the optimal adjustment of the measuring parameters and can be further enlarged it is also applicable for other analytical tasks and instruments.
4. To fractionate heavy metal content of sediments, I compared the information contents of the EU BCR recommendation and of the „SFE” method developed by SZIE (extraction made by CO₂ and H₂O solvents in supercritical extractor and by their combinations). I

found out the following: the results of the extraction steps carrying similar chemical information are comparable (BCR 1. step / sum of (H₂O/CO₂) 2. and 3. steps). With the SFE method the water-soluble fraction and the fraction bound to carbonates can be separately determined; the BCR method indicates these together in the fraction dissolvable by acetic acid. This validation substantiated the further improvement of the method and the extension of its application field, which since the finishing of my work has taken place to soil and gravitation dust samples.

8. Conclusions and suggestions

In the course of my work I proved that in the case of gas-generating sample introduction, the microwave-induced plasma optical emission spectrometry is well applicable element specific detector for stable nitrogen isotopic speciation.

Also in the case of HPLC separation the MIP-OES proved applicable to element-specific detection. However, in this case, the sample-introduction problems arising from the limited thermal capacity of MIP limit the performance of the method.

With the further development of the MIP-OES, with the establishment of new resonator constructions and with the miniaturisation of the sample-introduction, the application possibility of the MIP-OES element specific detection can be improved too in this field. I suggest that the researches should be continued primarily in this direction henceforward. Another further research area could be the extension of the application to other elements, such as the speciation of phosphorus.

The sequential extraction method based on the subcritical water and the supercritical CO₂ and on their combinations proved well applicable to determine the water-soluble element content being able to mobilize in the form of hydro-carbonate. The extraction times should though be optimised to the different types of samples depending on the function of carbonate content.

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