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Analysis of environmental samples by oaTOF-ICP-MS

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ABSTRACT

This work deals with an analysis of environmental samples by mass spectrometry using ionization in inductively coupled plasma. A mass spectrometer with orthogonal acceleration of ions and time-of-flight analyzer was used. This spectrometer offers some unique parameters such as ultimate speed of the analysis, simultaneous record of full mass spectra and increased precision in measuring of isotopic ratios across the whole mass spectrum. These features can be used for fast analysis of a high number of samples, for multi-elemental analysis of low volume samples or for statistical treatment of large data sets using fully isotopic information.

Elaborated methods of oaTOF-ICP-MS were used for analysis of horse hair, differently grown carrots and a new simple method for the analysis of low volume samples was developed as well.

ABSTRAKT

Práce se zabývá problematikou analýzy environmentálních vzorků s využitím metody hmotnostní spektrometrie s ionizací v indukčně vázaném plazmatu. Byl použit hmotnostní spektrometr s průletovým analyzátorem a ortogonálním urychlováním iontů. Toto řešení nabízí některé unikátní parametry jako je extrémní rychlost analýzy, simultánní záznam plných hmotnostních spekter nebo zvýšená přesnost měření izotopických poměrů přes celé hmotnostní spektrum. Tyto vlastnosti je pak možné využít například pro rychlou analýzu velkého počtu vzorků, pro multiprvkovou analýzu vzorků o velmi malém objemu, nebo pro statistické analýzy větších souborů vzorků, kde se využívá komplexní izotopická informace.

Vypracované metody oaTOF-ICP-MS byly použity pro analýzu koňských žíní, různě pěstovaných mrkví a rovněž byla vyvinuta nová jednoduchá metodika pro analýzu vzorků o malém objemu.

KEYWORDS

oaTOF-ICP-MS, multielemental analysis, environmental samples, isotopic ratios determination, statistical data treatment, horse hair, carrot, low volume samples.

KLÍČOVÁ SLOVA

oaTOF-ICP-MS, multiprvková analýza, environmentální vzorky, izotopová analýza, statistické zpracování dat, koňské žíně, mrkev, analýza malých vzorků.

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Introduction

An elemental analysis of environmental samples belongs among basic indicators of condition of the environment. The most frequent reasons for an analysis of such samples are to reveal a contamination and anthropogenic influence on the environment. According to the state, we can distinguished between solid, liquid and gas environmental samples. The frame of this work deals with liquid and solid samples only. Atomic spectrometry methods are often used for an elemental analysis of liquid and solid samples. Among these methods, belongs atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence techniques (XRF), modifications of mentioned and others. This dissertation deals with preparation of methods and analysis of environmental samples by oaTOF-ICP-MS (inductively coupled plasma mass spectrometry with orthogonal acceleration of ions and time-of-flight mass analyzer).

1 Theory

1.1 Inorganic mass spectrometry

Inorganic mass spectrometry is a technique discovered in the first half of the twentieth century. The first work on analysis by mass spectrometry was published in 1934 by Dempster. However, broader application for elemental analysis was achieved much later, in the 1980s, mainly thanks to inductively coupled plasma (ICP) as an ion source. [1] Inorganic mass spectrometry is now widely used for very sensitive, accurate, fast, trace and ultratrace analysis of elements (even isotopes and their ratios) in different matrices. These matrices can be of any state of matter (liquid, solid or gaseous). [2-4] Inorganic mass spectrometry plays an important role in the analysis of highly pure materials: metals [5-8], alloys [9], semiconductors [10-13], insulators [14-16], etc., technical materials: nitrides, carbides [16-19], environmental samples: water [20-22], biological materials [23-25], geological samples [26-28] and others. Last but not least the MS technique is also utilized for analysis of radioactive materials [29-33]. The basic principle of inorganic mass spectrometry can be seen in the following scheme:

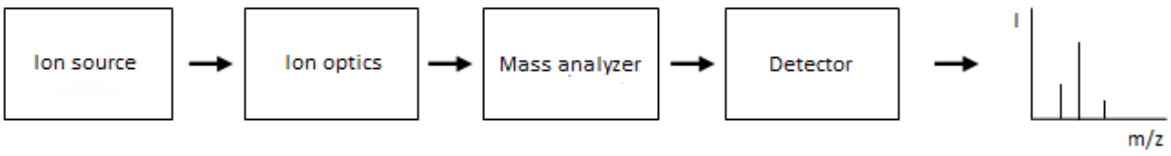


Figure 1.: Basic scheme of inorganic mass spectrometry [1]

Several different techniques can be used as an ion source. The Inductively coupled plasma ion source (ICP) will be described in more detail in the following chapter (1.1.1). The ion source serves for evaporation, atomization and subsequent ionization of the sample. The resulting ions are further sampled using a multistage interface that

separates normal pressure and vacuum part of the spectrometer. The ion beam is further modulated and transported towards the mass analyzer by ion optics. The mass analyzer separates ions according to their effective mass m/z (mass to charge ratio). The separation of the ions is based on different principles. The principle of the time-of-flight mass spectrometer used in the application part of the dissertation will be described in chapter (1.1.2). Separated ions raised from the mass analyzer continue to the detector where they are recorded. A mass spectrum is acquired, where the effective mass corresponds to the respective isotope of the element and the peak intensity represents its concentration. We are able to determine not only the concentration of literally all elements of the periodic table but also their possible isotopes by mass spectrometry. [1]

1.1.1 Ion sources in inorganic mass spectrometry

Inorganic mass spectrometry uses a number of ion sources. The oldest technique used for ionization of the sample (in conjunction with MS) is the Spark Source Mass Spectrometry (SSMS). The ionization of the sample is carried out by high-temperature spark in a vacuum. [1,34-37]. Other ionization techniques in connection with MS include: Sputtered Neutral Mass Spectrometry (SNMP) [38,39], Laser Ionization Mass Spectrometry (LIMS) [40,41], Resonance Ionization Mass Spectrometry (RIMS) [42,43], Glow Discharge Mass Spectrometry (GDMS) [44,45], Secondary Ion Mass Spectrometry (SIMS) [46,47], Thermal Ionization Mass Spectrometry (TIMS) [48,49], Accelerator Mass Spectrometry (AMS) [50,51] and generally the most commonly used Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique. [25, 52-54]

- **ICP (inductively coupled plasma) ion source**

The first connection of the mass spectrometer with ICP as an ion source is attributed to English scientist (Gray) in 1975. [2,3] In 1980, the first ICP-MS publication was produced [55] and in 1983 the first commercially available ICP-MS spectrometer (Sciex, Canada) appeared. [1,56] Some other producers soon emerged and the technique quickly became a significant player in the field of multi-elemental trace and ultratrace analysis of all types of matrices. ICP-MS has gained its status and popularity mainly due to its features such as: high sensitivity, high reproducibility and stability of results, trace and ultratrace multi-elemental capability, wide dynamic range, high throughput and ability to measure isotopic ratios. [56] Another advantage of using ICP is an introduction of a sample into plasma at atmospheric pressure. This can be useful for connection with Flow Injection Analysis (FIA), High Performance Liquid Chromatography (HPLC), Electrothermal Vaporation (ETV), or Laser Ablation (LA) and others. [3] Inductively coupled plasma used as an ion source in mass spectrometry is practically identical to the ICP used in ICP-OES. Argon is the most commonly used plasma gas. The plasma is generated by a radio frequency magnetic field. The high-frequency current (typically 27.12 or 40.68 MHz) is fed to an induction coil located at the end of a quartz plasma torch. Plasma ignition is initiated by a high voltage spark. The constant movement of electrons and ions is induced by the oscillating magnetic field. This leads to collisions with Ar atoms and to the so-called ohmic heating of the gas resulting in plasma formation and temperatures up to

10,000 K. The plasma is generated at atmospheric pressure, typically between 0.75 and 1.6 kW. High-frequency generators that use 27.12 MHz have higher outputs (up to about 2 kW). [56]

After the ignition, the plasma receives an ellipsoidal shape. Upon increasing the flow of the carrier gas, a characteristic toroidal shape is formed. In the central plasma channel, the temperature is lower than in the induction zone. The ionization of the analyte ($M \rightarrow M^+ + e^-$) in plasma is achieved by several mechanisms. Those include electron impact ionization, charge transfer ionization and so-called Penning ionization. It was calculated that at a temperature T = 7500 K (electron density = $1x10^{15}.cm^{-3}$), ≥ 90% ionization occurs for 54 elements of the periodic table (to the first ionization stage). All elements with the first ionization energy $E_{ion} \leq 10$ eV ionize from ≥ 50%. Only 3 elements (He, F, Ne) have the first ionization energy so high, that they will not be ionized by the plasma and cannot be measured by ICP-MS. [56]

Furthermore a small percentage of double-charged and polyatomic ions are formed in plasma. Double-charged ions are represented mainly by elements with low ionization energy, including barium and rare earth elements. ICP is therefore a very effective ion source for subsequent MS detection. [56]

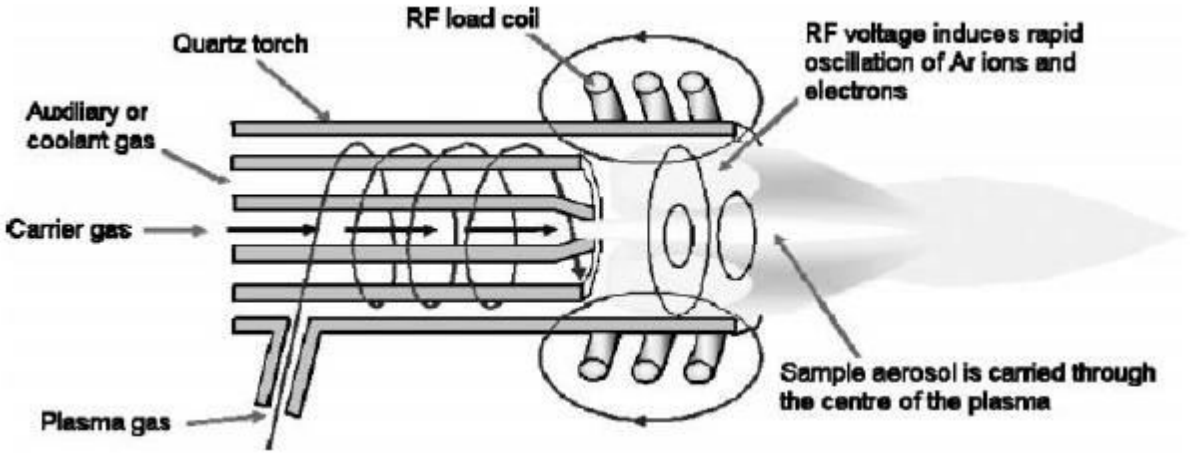


Figure 2.: ICP Ion Source [56]

1.1.2 Mass analyzers commonly used with ICP ion source

Nowadays, we can distinguish several types of inorganic mass analyzers using ICP as an ion source. The most important mass analyzers, according to the ion separation principle, are quadrupole mass analyzers (QMS) [10,31,57,58], sector field mass analyzers (SFMS) [22,59-61] and time-of-flight mass analyzers (TOF-MS) [62,63]. Among other less common analyzers, we can include mass spectrometers using either an ion trap to separate ions (ITMS) [64], or ionic cyclotron resonance with Furier Transformation (FTICRMS) [65]. Quadrupole mass analyzers serve as mass filters and allow only certain effective mass m/z to pass through the quadrupole analyzer. The remaining ions are repelled. Sector field mass analyzers use magnetic and electric fields to focus an ion beam with a specific m/z on a precisely defined part of the analyzer (exit slit). The detector of ions is located behind the exit slit. By changing

magnetic and electric field parameters, the ions of different m/z pass through the slit and we can obtain the entire mass spectrum. We are talking about scanning devices, which again act as a mass filter. Another option utilizing the electric and magnetic fields to filter the ions, is to use a series of tightly adjustable slits and detectors. Then we can simultaneously record multiple ions. We are talking about so-called multi-collector analyzers which are mainly used for accurate measurement of isotopic ratios. Time-of-flight mass analyzers are equipped with a drift tube where ions reach different speeds based on their m/z. The lighter ions reach higher velocities and thus hit the detector earlier. The mass spectrum is obtained by measuring the incident ions over time. [56]

- **Time-of-flight mass analyzers**

Mass spectrometers with TOF analyzers are the easiest spectrometers in design and are the youngest improvement in a group of inorganic mass analyzers. [56] The basic concept of TOF-MS has been described by Wiley and McLaren in the 1950s [66]. However, an important development triggered two events much later in the 1990s. The first was the development of Matrix Assisted Laser Desorption Ionization (MALDI), where the TOF-MS analyzer is highly suitable. The second was the "rediscovery" of the TOF-MS technique using orthogonal acceleration of ions, which was described in 1989 by Guilhaus and Dodonov. [67]

The ions generated in ICP are sampled through a multiple interface that separates the normal pressure and the vacuum region. Extracted ions are further modulated by a set of electrodes forming so-called ion optics. The ions coming into the accelerator section are accelerated into the drift tube by potential pulse. Since all accelerated ions received an equal potential pulse they also achieve the same kinetic energy Ek. According to the equation for kinetic energy: $Ek = 0.5.\ mv^2$ [68] it is clearly seen that ions of different m/z will have different speeds. The time they need to reach the detector is directly proportional to the square root of their masses. Based on that, light ions reach the detector earlier, heavier ions later. When the drift region is about one meter long, even the heaviest ions reach the detector in about 50 µs. This means that TOF-MS is capable of measuring 20-30 thousand full mass spectra in one second. TOF-MS is much faster (2-3 orders of magnitude) than conventional quadrupole systems measuring in scanning mode. According to the method of ion acceleration to the drift tube, two types of commercially available TOF spectrometers (orthogonal acceleration TOF (oaTOF) and axial ion acceleration (linear TOF)) can be distinguished.[56]

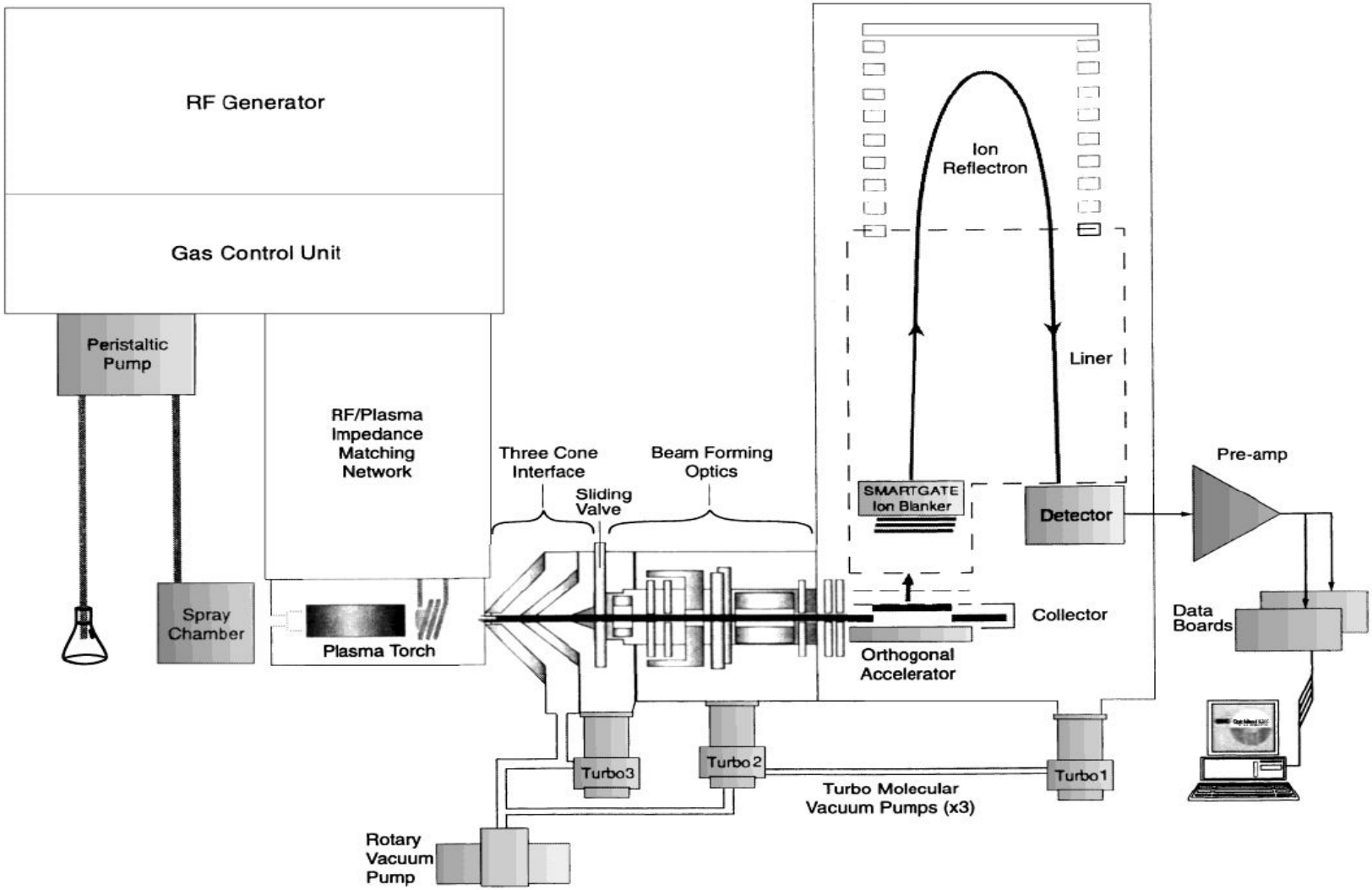


Figure 3.: Scheme of oaTOF-ICP-MS, Optimass 8000 (GBC Scientific Equipment) [67]

2 Goals of the dissertation

The Main goal of the presented dissertation was preparation, optimization and application of methods for multi-elemental analysis of various environmental samples by inductively coupled plasma mass spectrometry with orthogonal acceleration of ions and time-of-flight analyser (oaTOF-ICP-MS). This technique represents an effective tool for very fast multi-elemental analysis without affecting isotopic ratios. These features are especially important when time-consuming multi-elemental analysis of large number of samples must be carried out. Furthermore, the oaTOF-ICP-MS technique is also beneficial in handling low volume samples or for provenance and comparative studies where non-affected isotopic ratios play an important role, etc. Very well prepared methods including sample collection, pre-treatment and analysis itself are crucial to acquire precise and accurate results. The main goal is further divided into three partial goals as follows.

- **Part 1.**

The first part of the dissertation deals with horse hair analysis. The goal was to collect, pre-treat and analyse horse hair samples (including optimization of all the mentioned processes). Part one should prove the relevance of such a technique and create methods to get valuable data for biomonitoring and statistical studies

- **Part 2.**

Goal number two was to compare different cultivation systems for growing carrots. We investigated three systems: conventional, organic (“bio”) and system of small growers. Systems were compared according to the elemental composition (nutrients, micro- nutrients, toxic metals, etc.), dry matter and nitrate content. In the first stage, it was necessary to obtain a large number of conventionally available samples, samples with the trademark "bio" and samples from small growers. The task was to create sufficiently large sample sets of individual cultivation systems for subsequent analysis and statistical evaluation of the differences. It was also necessary to develop a method for sample processing and the ICP-OES and oaTOF-ICP-MS analysis itself. The subsequent goal was to analyse samples and statistically process the obtained large data. The final task was to compare individual growing systems based on statistical analysis and compare gained extensive data with legislation and available literature.

- **Part 3.**

The third and final task was to build up a technique and develop a unique method for introducing of low volume samples into the oaTOF-ICP-MS instrument. It was also necessary to test this conjunction, to determine its characteristics, to optimize the proposed method, and to validate on different types of environmental matrices.

3 Applications of oaTOF-ICP-MS

3.1 High-throughput multi-elemental analysis of horse hair

3.1.1 Introduction

An analysis of hair is frequently utilized to assess the impact of the environment or diet habits on the state of health of organism (biomonitoring of pollutant´s exposition and bioaccumulation studies). History of hair analysis goes back to the 19th Century. Hair tissue presents a very specific tool when considering intoxication of an organism by various elements (As, Cd, etc.) or by organic compounds such as PCDD, PCDF, PCB, PAH, THC, barbiturates and so on. Trace elements, minerals, drugs, toxins and their metabolites are incorporated into the structure of hair and can be determined even a long time after an organism's death. Usually a hair stem presents information about exposition of drugs or other chemicals several months or years retrospectively and a hair root reveals an actual exposition (Dunnett & Lees, 2003) [69].

A contamination of hair can be divided into an exogenous and an endogenous contamination. An endogenous contamination originates from food or environment (air, dust, smoke, cosmetics). Endogenous contaminants are a result of a long-term exposure, when they enter an organism in several ways such as respiration, alimentary route, or through skin. They are built into the hair structure during growth of the individual. Exogenous, also known as surface contaminants, stick to the skin or hair and can be easily removed by washing processes (Asano et al., 2006) [70]. For long-term contamination, hair profiles are suitable, while analysis of hair roots can demonstrate acute intoxication (Rodushkin & Axelsson, 2000) [71]. Hair is a non-invasive and readily available matrix, easily treatable without any special storage requirements (Esteban & Castano, 2009) [72].

One of the most important steps in any analysis is the way of sample preparation. It can seriously affect the results of analysis. Gentle, but exact removing of an exogenous contamination prior an analysis is emphasized. Practically, a lot of washing procedures were tested using Triton (1:200), isopropyl alcohol and acetone (Asano et al., 2002) [73]. Washing in an alkaline solution tetramethylamonium hydroxide was employed by (Rodrigues et al., 2008) [74], as well as washing in various concentrated (0.1 to 2%) solution of Triton (Sobanska, 2005) [75] or using a combination of nitric acid and hydrofluoric acid (Dunnett & Lees, 2003) [69]. The most widespread approach of sample preparation of hair is washing in nitric acid and in Triton, followed by microwave digestion in various mixtures of HNO_3 and H_2O_2, HNO_3 and HCl, HNO_3 and HF (Rodushkin & Axelsson, 2000 [71]; Rao et al., 2002 [76]) whose choice depends on the analytical detection technique used.

Nowadays, for the elemental analysis of hair the most common methods utilized are ICP-OES (inductively coupled plasma optical emission spectrometry) (Rao et al., 2002 [76]; Chojnacka et al., 2005 [77]), ET-AAS (atomic absorption spectrometry with electrothermal atomization) (Ribeiro et al., 2000 [78]; Baysal & Akman 2010 [79]) and ICP-MS (inductively coupled plasma mass spectrometry) (Chojnacka et al., 2005 [77]; Madejón et al., 2009 [80]). Another analytical technique employed for hair

analysis is PIXE (particle induced x-ray emission spectrometry) which does not require complicated sample preparation (Assano et al., 2006 [70]), or INAA (Instrumental neutron activation analysis). INNA involves a minimum sample handling as well (Armelin et al., 2001 [81]). LA-ICP-MS (laser ablation ICP-MS) method can be used for rapid identification and screening of toxic and nutritious elements in hair and does not need time consuming sample preparation. Steely et al (2007) [82] used LA-ICP-MS for analysis of ^{75}As, ^{64}Zn and ^{208}Pb in human hair to differ them according to their origin. They demonstrated that LA-ICP-MS can be used to obtain rapid qualitative and quantitative identification of arsenic in a single strand of human hair as a bio-indicator tissue.

The aim of the first part of this work was to collect, optimize pre-treatment, prepare and analyze horsehair samples. Emphasis was put on the elaboration of a complex multi-elemental oaTOF-ICP-MS method. This study highlights the use of this technique in cases where multi-elemental analysis of a large number of environmental samples is required. Obtained extensive data can be used for statistical processing and isotope studies due to the simultaneous recording of the entire mass spectrum.

3.1.2 Results and discussions

- **Optimization of the sample preparation procedure**

Before a decomposition step, removing of exogenous contaminants from hair surface is necessary. A washing procedure has to be effective in washing down of outer impurities - and gentle in order not to interfere with internal hair volume. In general, there is not any cleaning strategy to strictly separate exogenous from endogenous contaminants. Three procedures were tested which consisted of consequent washing with nitric acid, acetone and Triton X-100, their mixtures, and distilled water. In this case, a working sample of black, non-dyed woman's hair was used. The washing sequence consisted of four steps with different washing agents. The processes utilized acetone, 0.1 M HNO_3, 1% Triton X-100 and ultrasonic bath. One gram of sample was supplemented with 50 mL of an appropriate washing solution in a 100 ml plastic bottle and inserted into an ultrasonic bath for a defined time. The following washing process has been assessed as the best: 10 min sonification in acetone, 10 min in water, 10 min in 0.1% HNO_3 together with 1% Triton and finally 10 min sonification in water. Washed and dried samples were digested using a microwave digestion system and analyzed using the oaTOF-ICP-MS method. Added volumes of washing agents were always 50 mL. The choice of optimal washing process was based on an analysis of rinse waters and washed/digested hair samples. In the rinse waters, levels of rinsed elements were evaluated. In the digested hair samples, contents of remaining elements were determined. Comparison of our results obtained from the tested washing processes showed that the best approach is the procedure, which includes the washing step with a mixture of 0.1 M HNO_3 and Triton X-100. To develop an appropriate washing strategy proved to be very difficult. Even with large number of data obtained, the statistical evaluation of the washing processes tested did not bring a clear verdict. The final decision was made based on the best recoveries for five parallel samples washed. The best washing strategy yields the highest recoveries, ranged in 93–105%, for all the elements determined. We are aware this approach does

not have to be necessarily the best for the accurate information about elemental composition, but it should be sufficient enough to have the results biased in the same way in all samples. It is believed that such washing procedure should not interfere with valuable information, which can be used in statistical treatment. The choice of suitable isotopes was a very important step due to differences in sample matrices. Working isotopes have been selected with a regard to possible isobaric overlaps of interfering ions with the same mass. Their choice was carried out using both a spectral library integrated in equipment software, and mass spectra of samples.

- **Method validation**

The validation of the proposed method was achieved by analysis of certified reference material Human Hair NCS ZC 8100 and by standard addition technique. The results of analysis of reference material shows a good match with certified values (see Table 1). The standard addition technique as a second validation method for elements non-certified in reference material was employed. Deviation of directions of calibration curves and curves plotted from standard additions ranged in 10% for all the determined elements except for Au. The limits of detection (LOD) of the used techniques were based on the triple of standard deviation of background counts for five blank solutions. The limits of detection of the whole method (LODm) were calculated from limits of detection for this technique multiplied by sample dilution. Detection limits of the proposed method ranged from 0.13 mg kg^{-1} (Eu, Gd, Tm) to 27.9 mg kg^{-1} (Au), except for Ni (48.5 mg kg^{-1}) which was probably affected by contamination raised from nickel cones.

Element	Isotope (amu)	Certified (mg kg^{-1})	Found (mg kg^{-1})	Recoveries (%)
As	75	0.198 ± 0.023	0.186 ± 0.006	91–97
Cd	114	0.072 ± 0.010	0.085 ± 0.007	108–128
Co	59	0.153 ± 0.015	0.146 ± 0.042	68–123
Cr	52	8.74 ± 0.97	8.700 ± 3.10	64–135
Pb	206 + 207 + 208	3.83 ± 0.18	3.684 ± 0.33	88–105
Sb	123	0.12 ± 0.002	0.118 ± 0.026	77–120

Table 1.: Validation data for analysis of horse hair by oaTOF-ICP-MS method (CRM - Human Hair NCS ZC 8100)

- **Throughput and method evaluation**

One hundred of horse hair samples were collected and prepared for multi-elemental analysis by oaTOF-ICP-MS according to above mentioned procedures. The first step of sample preparation was the washing process. As the best washing strategy, we chose the process that incorporated washing in Triton. The decision was made according to highest recoveries for five replicates of one tested sample (93–105%). Reproducibility of the mentioned washing strategy was very high and it is believed that valuable information, which could be obtained from isotopic ratios, persists. Typical washing throughput was 20 samples per hour. Washed samples were let dried for 24 h (laboratory temperature). Microwave digestion was then optimized to have

throughput of 24 (23 samples and 1 blank) positions per hour. As an analytical technique inductively coupled plasma time-of-flight mass spectrometry with orthogonal acceleration of ions was utilized. In comparison with other technique, oaTOF-ICP-MS has an advantage of very low detection limits and very fast analysis with fully isotopic information in one time. This is particularly important when a large number of low volume samples with a number of elements to be determined are analyzed. Another reason why to use such a technique is the very precise isotopic ratio obtained. When using ICP-OES for this kind of analysis, one can have a very fast multi-elemental method but insufficient detection limits for trace elements and impossibility to get isotopic information. In the case when XRF techniques are employed you can avoid time-consuming sample digestion. Unfortunately, XRF does not provide isotopic information and the detection limits are poor. Electrochemistry and AAS are not considered as fast methods, and therefore, mass spectrometry remains suitable. Mass spectrometry methods are well-known to have superior detection limits and capability to measure isotopes. Quadrupole and sector field mass spectrometers have excellent detection power but they are not fast, and therefore, isotopic ratios can be affected because of fluctuation during analysis. Moreover, when analysing low volume samples, it is impossible to get full isotopic information. Chosen oaTOF-ICP-MS has the features of very fast multi-elemental analysis with unaffected isotopic ratios and very low detection limits. All the samples were analyzed as duplicates and results were averaged. One sample sequence consists of 30 real samples (15 duplicates), calibration, recalibration after every ten samples, and check sample after every 20 sample. Ranges of determined elements are depictured in figure 4. Relative standard deviation for all samples and determined elements did not exceed 10%. This large data set was subsequently used for statistical evaluation which is not a part of this dissertation. A sample consumption of 0.7 ml, for determination of unlimited number of isotopes in one duplicate, was accomplished. Acquisition time for one of the duplicates was three times 5 s. To avoid cross-contamination between samples, a rinse time of 120 s was used. We were monitoring response on all the utilized isotopes for a highly concentrated sample and found that after 2 min of rinsing, any signal dropped to the baseline. We achieved a high throughput method of one hundred of samples per six hours (without sample preparation). High throughput is very important for large batches of samples which are intended for biomonitoring and statistical studies.

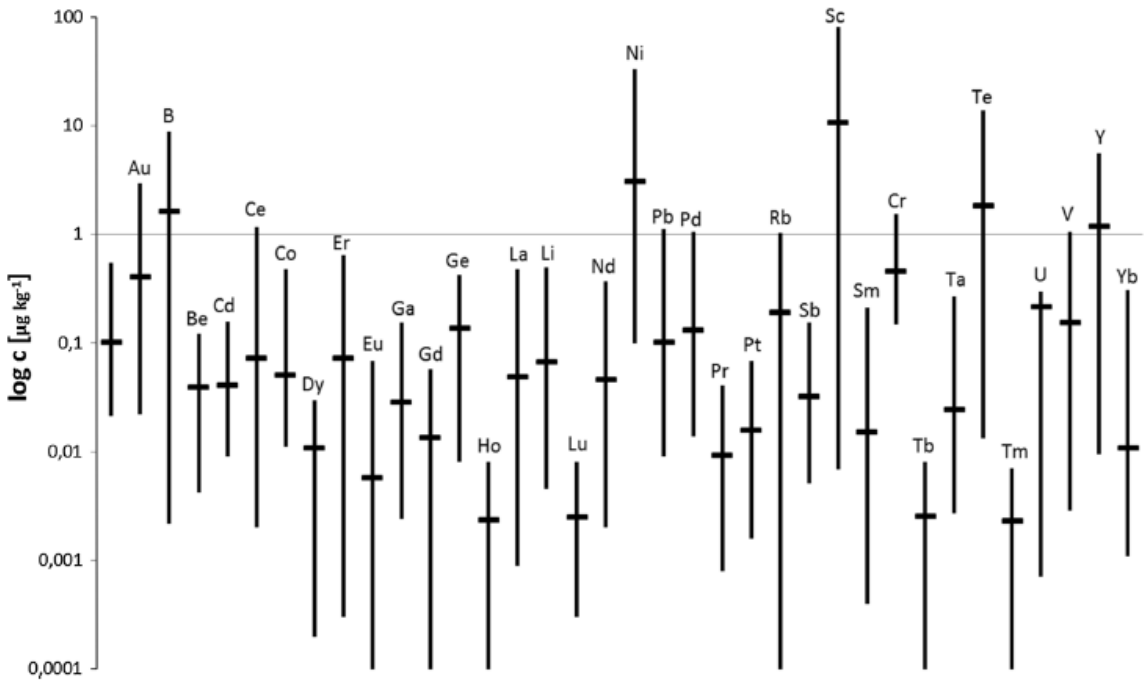


Figure 4.: Concentration ranges (in logarithmic scale) of 36 elements determined in one hundred horse hair samples

3.2 Elemental analysis of differently grown carrots

3.2.1 Introduction

The rising consumption of organic food in recent years is associated with increasing consumer interest in the safety and quality of foods. Organic foods are generally perceived as healthier and safer than conventional ones. Moreover, the organic production provides agronomic and environmental benefits such as preservation of natural resources and reduction of air, water, soil and food pollution (Herencia, Garcia-Galavis, Dorado & Maqueda, 2011 [83]; Soltoft, Bysted, Madsen, Mark, Bugel, Nielsen & Knuthsen, 2010 [84]; Domagała-Świątkiewicz & Gastoł, 2012 [85]). Intake of organic foods can have certain advantages such as the ingestion of more phenolic compounds, vitamins, and less of nitrates and pesticides (Lima & Vianello, 2011 [86]). Organic foodstuffs are reported to contain higher concentrations of nutritionally beneficial trace metals and lower concentrations of dangerous heavy metals (Kelly & Bateman, 2010 [87]). According to Hoefkens et al, the quality of organic and conventional products is often discussed without clear conclusions. Only a limited number of studies on nutrient and/or contaminant are “paired” for organic and conventional vegetables have been undertaken, and they are of moderate or poor quality (Hoefkens, Vandekinderen, De Meulenaer, Devlieghere, Baert, Sioen, De Henauw, Verbeke & Van Camp, 2009 [87]; Soltoft, Bysted, Madsen, Mark, Bugel, Nielsen & Knuthsen, 2010 [84]).

Organic vegetables are often compared with conventional ones in terms of chemical composition in connection with soil composition (Kawada, Lee, Suzuki & Rivai, 2002 [89]). Similarly, nutritional, sensory, taste and agricultural aspects are followed in connection with fertilizing, irrigation, pollution etc. (Maqueda, Herencia, Ruiz & Hidalgo, 2010 [90]).

An elemental fingerprint analysis can also serve as descriptors of the geographical origin and has the potential to enable the authentication of organic crops (Kelly & Bateman, 2010 [87]). It was used, e.g., for classification of winter wheat, spring barley, faba bean, and potato (Laursen, Schjoerring, Olesen, Askegaard, Halekoh & Husted, 2011 [91]), honeys (Chua, Abdul-Rahaman, Sarmidi & Aziz, 2012 [92]), virgin olive oil, etc.

The aim of this partial goal was to collect, prepare and analyze samples of differently grown carrots (organically ("bio"), conventionally, privately cultivated (self-grown or domestic production)). The purpose of the analysis was the subsequent statistical evaluation and comparison of individual growing systems. They were compared depending on the content of the macro and micro elements, contaminants, dry matter and nitrates. It was also necessary to develop and apply methods for elemental analysis by ICP-OES and oaTOF-ICP-MS. Carrot samples were collected during autumn 2012 and spring 2013.

3.2.2 Results and discussions

Na, K, Mg, Ca, P, S, B, Al, Mn, Zn, Fe, Cu, Cr, Ni, Pb, Cd, As, Hg, nitrates and DM contents in differently grown carrots were statistically processed. The median, average, standard deviation, minimum, and maximum values were calculated for single origins, i.e. the growing systems. Obtained concentrations were compared with available literal data, limits for food contaminants, and the RDIs (the Czech Republic, 2016, 2008, 2004 [93 – 95]).

- **The Results for single parameters**

Our results for the above listed parameters were compared with the data available for some of nutritional elements / contaminants, which were occasionally published in regards to the growing system; but rarely with respect to the soil composition or the local contamination.

The **dry matter** is a significant factor (depending on a variety, watering, way and length of storage, etc.), which can lead to misinterpreting the analytical results and related information on nutritional values or safety. Therefore, it is necessary to indicate, if the results are expressed on a dry or fresh weight basis. In some publications, this figure is not listed, or results based on the dry or fresh matter are mixed, and unclearly (Warman & Havard, 1997 [96]). All our results were related to the fresh weight. The DM varied over a range of 7.15 – 13.6 % for conventional, 6.74 – 15.6 % for organic and 6.6 – 20.3 % for self-grown carrots. Our results correspond to the data from the literature: 12.17 – 13.63 % for certain carrot varieties (Silva, Vieira,

Vieira, Amboni, Amante & Teixeira, 2007 [97]), and 10.7 – 11.0 % for other carrots (Masamba & Nguyen, 2008 [98]).

Nitrates in a crop are usually given in relation to fertilizers, and heat / light conditions. Nitrates varied (all in mg kg^{-1}) from non-detectable (8.9) to 4110 for the conventional, to 2180 for organic and 6030 for self-grown carrots. According to a meta-analysis, nitrate was significantly lower in organic (45) than in conventional carrots (171) (Hoefkens, Vandekinderen, De Meulenaer, Devlieghere, Baert, Sioen, De Henauw, Verbeke & Van Camp, 2009 [88]).

Carrots are considered to be "a low **sodium** content" vegetable: we found (all in mg kg^{-1}) 57.3 - 1150 for conventional, 98.5 - 651 for organic and 58.1 - 1950 for self-grown carrots. 1170 - 4640 was reported for conventional and 1170 - 4980 for organic carrots (Warman & Havard, 1997 [96]). The Czech Food Composition Database (CFCD) provides the value of 80 mg Na in 100 g of the edible part (Centre for Food Composition Database, 2016 [93]).

The content of **potassium** was presented (all in mg kg^{-1}): 2070 for organic and 2730 for conventional (Hoefkens, Vandekinderen, De Meulenaer, Devlieghere, Baert, Sioen, De Henauw, Verbeke & Van Camp, 2009 [88]); 3027 for conventional and 3268 for organic (Masamba & Nguyen, 2008 [98]), 22900 – 24700 for conventional and 24600 - 41700 for organic samples (Warman & Havard, 1997 [96]). Our results show 1460 – 6780 for conventional samples, 2020 – 7610 for organic ones and 1500 – 11400 for self-grown carrots. According to the CFCD, carrots contain 276 mg of potassium in 100 g of the edible part (Centre for Food Composition Database, 2016 [93]).

Our results for **calcium** (all in mg kg^{-1}) were 220 – 870 for conventional, 220 – 678 for organic and 248 – 970 for self-grown samples. In literature, 230 for organic and 260 for conventional (Hoefkens, Vandekinderen, De Meulenaer, Devlieghere, Baert, Sioen, De Henauw, Verbeke & Van Camp, 2009 [88]), 363 for organic and 317 for conventional (Masamba & Nguyen, 2008 [98]) and an order of magnitude difference 3250 – 3790 for organic and 3110 – 3890 for conventional were reported (Warman & Havard, 1997 [96]). The CFCD provides 41 mg of calcium in 100 g of the edible part (Centre for Food Composition Database, 2016 [93]).

Our **magnesium** (all in mg kg^{-1}) in carrots was 49.1 – 213 for conventional, 52.4 – 195 for organic and 58.7 – 306 for self-grown compared to 1000 – 1470 for conventional and 1050 – 1570 for organic (Warman & Havard, 1997 [96]). The CFCD declares 18 mg of magnesium in 100 g of the edible part (Centre for Food Composition Database, 2016 [93]).

In our study (all in mg kg^{-1}), **phosphorus** was found 156 – 701 for conventional, 219 – 915 for organic and 205 – 1230 for self-grown carrots. Values 2230 – 3280 for organic comparable with 2330 - 3260 for conventional were reported (Warman & Havard, 1997 [96]). The CFCD declares 35 mg of phosphorus in 100 g of the edible part (Centre for Food Composition Database, 2016 [93]).

The content of **sulphur** was referred (all in mg kg^{-1}) 2960 – 5200 for organic and 2340 – 4100 for conventional carrots (Warman & Havard, 1997 [96]). We found lower results in about one order of magnitude: 23.5 – 701 for conventional, 74.0 – 255 for organic and 73.2 – 405 for self-grown samples.

In the case of **boron**, the contents were observed (all in mg kg^{-1}) from undetectable (2.3) to 4.76 (conventional), 6.66 (organic) and 5.73 mg kg^{-1} (self-grown). Our results are lower in comparison with the data from literature: 16.8 – 19.4 (conventional) and 18.6 - 219 (organic; Warman & Havard, 1997 [96]).

Our results for **manganese** were (all in mg kg^{-1}) from undetectable (0.53) to 9.39 for conventional, to 2.45 for organic and to 8.38 for self-grown carrots. 14.8 – 24.6 for conventional and 12.0 – 22.2 for organic was reported (Warman & Havard, 1997 [96]).

Next elements (iron, zinc, copper) are mentioned as both a significant nutrient and a potential contaminant. In our study **iron** was seen (all in mg kg^{-1}) 1.25 – 15.8 for conventional, from undetectable (i.e. 0.58) to 31.0 for organic and 2.54 – 71.2 for self-grown carrots. Iron is reported 20.0 – 36.0 for conventional and 24.0 – 29.2 for organic carrots (Warman & Havard, 1997 [96]). The CFCD declares 1.1 mg of iron in 100 g of the edible part (Centre for Food Composition Database, 2016 [93]).

Zinc was found (all in mg kg^{-1}) in the range from undetectable (0.43) to 18.9 for conventional, to 22.3 for organic and to 19.8 for self-grown carrots. In the literature, 24.0 – 26.0 for conventional and 21.0 – 24.8 for organic carrot (Warman & Havard, 1997 [96]) and 2.4 - 4.0 for carrots in Japan was reported (Kawada & Suzuki, 2011).

We estimated contents of **copper** (all in mg kg^{-1}) in the range from undetectable (0.075) to 5.35 for conventional, to 3.52 for organic and to 5.31 for self-grown carrots. 7.4 – 8.4 for conventional and 6.2 – 7.0 for organic carrots (Warman & Havard, 1997) and 0.7 – 1.0 in Japan carrots was observed (Kawada & Suzuki, 2011 [99]).

Additional elements discussed below are heavy metals considered toxic. Our results for **cadmium** (all in mg kg^{-1}) were from undetectable (0.013) to 0.126 for conventional, to 0.104 for organic and to 0.388 for self-grown carrots. In the literature, 0.022 for conventional and 0.026 for organic carrots (Hoefkens, Vandekinderen, De Meulenaer, Devlieghere, Baert, Sioen, De Henauw, Verbeke & Van Camp, 2009 [88]) and 0.002 – 0.179 and 0.2 mg kg^{-1} for Japan carrots was reported (Kawada & Suzuki, 2011 [99]).

Lead was determined (all in mg kg^{-1}) from undetectable (0.0063) to 1.01 for conventional, to 0.0990 for organic, and to 0.388 mg kg^{-1} for self-grown carrots. 0.105 for conventional and 0.263 for organic carrots came from the meta-analysis (Hoefkens, Vandekinderen, De Meulenaer, Devlieghere, Baert, Sioen, De Henauw, Verbeke & Van Camp, 2009 [88]).

In the study, the concentrations of **arsenic** (all in mg kg^{-1}) were found from undetectable (0.080) to 1.68 for conventional, to 0.777 for organic, and to 1.72 for self-grown samples. In Spanish carrots, 0.241 was published (Matos-Reyes, Cervera, Campos & de la Guardia, 2010 [100]).

There is lack of the literal data for the next elements in carrots. **Nickel** occurred (all in mg kg^{-1}) in our analysed carrots in the range from undetectable (0.088) to 6.86 for conventional, to 2.69 for organic and to 46.0 for self-grown samples. The content of **chromium** was from undetectable (0.088) to 0.355 for conventional, to 0.219 for organic, and to 39.8 mg kg^{-1} for self-grown carrots (all in mg kg^{-1}). In the case of **aluminium**, we found from undetectable (5.5) to 38.4 (conventional), 201 (organic) and 93.7 (self-grown; all in mg kg^{-1}). **Mercury** was extremely low, undetected in most samples, owing to the particularly low concentrations found with most of the values under the LOD_M. Mercury was excluded from the statistical evaluation.

Obtained extensive data were further compared with recommended daily intakes (RDIs) for carrots and statistically processed to reveal the differences based on the growing system and composition. The extremely contaminated samples were also discussed.

	RDI[a]	Limit[b]	A/B/C[c]	LOD_M	A–conventional/n = 71				B–organic/n = 71				C–self-grown/n = 76			
					Min.	Max.	$\tilde{x}$	$\bar{x} \pm s$	Min.	Max.	$\tilde{x}$	$\bar{x} \pm s$	Min.	Max.	$\tilde{x}$	$\bar{x} \pm s$
Na	200			5.3	57.3	1150	355	413 ± 250	98.5	651	261	280 ± 130	58.1	1950	266	417 ± 380
K	375			80	1460	6780	2710	2970 ± 1100	2020	7610	3230	3460 ± 1000	1500	11,400	5880	6150 ± 2000
Mg	800			0.83	49.1	213	104	114 ± 37	52.4	195	106	110 ± 32	58.7	306	182	179 ± 49
Ca	700			1.1	220	870	406	425 ± 150	220	687	456	450 ± 98	248	970	581	590 ± 160
P				5.8	156	701	304	315 ± 96	219	915	320	347 ± 130	205	1230	666	679 ± 190
S				5.5	23.5	327	182	189 ± 68	74.0	255	153	157 ± 42	73.2	405	218	228 ± 79
B				2.3	nd[e]	4.76	2.50	2.86 ± 0.61	nd[e]	6.66	2.51	2.84 ± 0.79	nd[e]	5.73	2.50	3.18 ± 1.0
Al	14			5.5	nd[e]	38.4	8.69	12.3 ± 7.0	nd[e]	201	13.3	18.5 ± 24	nd[e]	93.7	16.9	20.3 ± 14
Fe	2	50	0/0/1	0.58	1.25	15.8	3.95	5.24 ± 3.4	nd[e]	31.0	4.20	4.96 ± 4.2	2.54	71.2	10.1	13.1 ± 11
Mn	10			0.53	nd[e]	9.39	0.774	1.69 ± 1.8	nd[e]	2.45	0.529	0.835 ± 0.47	nd[e]	8.38	1.04	1.26 ± 1.1
Zn	4	25	0/0/0	0.43	nd[e]	18.9	5.69	6.10 ± 3.5	nd[e]	22.3	6.79	6.74 ± 3.7	nd[e]	19.8	6.36	6.91 ± 4.3
Cu		10	0/0/0	0.075	nd[e]	5.35	0.443	0.858 ± 1.1	nd[e]	3.52	0.376	0.568 ± 0.69	nd[e]	5.31	0.721	1.01 ± 1.1
Ni		2.5	3/2/3	0.088	nd[e]	6.86	1.44	1.58 ± 0.90	nd[e]	2.69	0.598	0.786 ± 0.64	nd[e]	46.0	0.369	1.23 ± 5.3
Cr		0.2	2/1/3	0.088	nd[e]	0.355	0.0459	0.0591 ± 0.053	nd[e]	0.219	0.0441	0.0463 ± 0.26	nd[e]	39.8	0.0100	0.548 ± 4.6
Pb		0.1	3/0/4	0.0063	nd[e]	1.01	0.0452	0.0641 ± 0.12	nd[e]	0.0990	0.0431	0.0429 ± 0.016	nd[e]	1.61	0.0152	0.0693 ± 0.26
As		0.5	2/1/3	0.080	nd[e]	1.68	0.0837	0.160 ± 0.27	nd[e]	0.777	0.0638	0.0774 ± 0.11	nd[e]	1.72	0.0270	0.163 ± 0.26
Cd		0.1	1/1/2	0.013	nd[e]	0.126	0.0682	0.0661 ± 0.025	nd[e]	0.104	0.0562	0.0600 ± 0.022	nd[e]	0.388	0.0244	0.0403 ± 0.053
NO_3^-		700	1/2/3	8.9	nd[e]	4110	8.00	97.8 ± 490	nd[e]	2180	1.0000	52.7 ± 270	nd[e]	6030	99.2	243 ± 710
DM[d]		–	–		7.15	13.6	9.59	9.88 ± 1.5	6.74	15.6	10.1	10.2 ± 1.6	6.60	20.3	11.3	11.7 ± 2.4

LOD_M–limit of detection of the whole analytical method, Min.–minimum value, Max.–maximum value, $\tilde{x}$–median, $\bar{x} \pm s$–mean value ± standard deviation.

[a] Recommended daily intake (Czech Republic, 2012).

[b] Limits for contaminants in food (Czech Republic, 2004).

[c] A/B/C–number of samples exceeding limit based on the sample growing method (A, conventional; B, organic; C, self-grown).

[d] Dry matter, in mg kg^{-1}.

[e] nd–not detected–result below the LOD.

Table 2.: RDIs, limits for contaminants in food, results for the analysed carrot samples (all in mg.kg^{-1}) and results for the statistical evaluation

3.3 Analysis of low volume samples by oaTOF-ICP-MS

3.3.1 Introduction

Elemental analysis of small samples is a very complex issue including careful sampling, sample pre-treatment and subsequent sensitive analysis. Handling a limited amount of samples is an integral part of many areas and is the subject of ongoing research. Among such areas belongs clinical, biological environmental, forensic analysis, etc. [101-103].

The pre-treatment of small samples before the subsequent analysis is a very important point in the process, and can be a major challenge. A small amount of sample material increases the risk of losses and contamination during individual analytical steps. According to the state, we most often encounter liquid or solid samples (that can be converted to liquid by various laboratory procedures). Low volume samples then represent substantial demands on the cleanliness of the environment, the laboratory glass ware, the chemicals used and the diligence of the analytical procedure in general [104].

The volume of the sample and the concentration of the analyzed elements have a major influence on the analytical techniques and methods to be used. Selected analytical techniques must have the ability to adapt the introduction system for low volume samples. Moreover, the sensitivity, speed, multi-elemental capability or simultaneous isotope analysis - to obtain an isotopic "fingerprint" (important for example in forensic analysis) can be advantageous.

Highly sensitive techniques that can be used to analyze small samples include, for example, atomic absorption spectrometry with electrothermal atomization (ETA-AAS) or inductively coupled plasma mass spectrometry (ICP-MS). This work is mainly focused on the ICP-MS technique and its modifications.

Depending on the number of elements to be analyzed and the selected ICP-MS technique, the analysis time is between 1 and 5 minutes (for the classical arrangement: peristaltic pump – nebulizer – spray chamber - ICP). Thus the volume of the sample consumed may range from 1 to 10 ml for analysis [102,103].

One of the simplest and easiest ways to reduce the amount of sample needed (ml → μL) is to reduce sample flow through the introduction system. However, with sample flow rates less than 100 $\mu L.min^{-1}$ a more efficient introduction system is required. This need is mainly due to processing small amounts of sample where any loss can cause severe reduction in sensitivity. Here are some stimuli that contributed to the development of such introduction systems [101,102,104].

- Less than 1 ml of sample is available
- Coupling ICP with capillary electrophoresis CE
- Reduction of interferences by lowering a solvent input

- Very small environmental, biological, clinical and forensic samples to be analysed
- Elimination of liquid waste (especially when analysing radioactive materials)

However, if we use one of the systems that reduce the amount of the sample a number of other factors, which are not so noticeable in the classical "bulk" introducing, must be taken into account [102].

- When using ICP techniques, an analytical signal is associated with the amount of analyte directly entering the plasma torch. This means that reducing the amount of the sample entering plasma must necessarily reduce the sensitivity of the method itself.
- Decreasing the flow rate of the sample through the system leads to much longer washing times. This is a particularly serious problem when switching between samples with different matrices.
- There is a significant reduction in transport efficiency when sample flow rate goes under 100 $\mu L.min^{-1}$

It is clearly seen that if we reduce the amount of sample flowing through the system, it is absolutely necessary to use a more efficient introduction technique. The Technique should be at least adapted to work with small volumes to maintain sufficient quality results. The advantage of such a technique can be higher signal stability, improved sensitivity, higher rate of analysis, reduced memory effects, reduced dead volumes, and a reduction of overall sample consumption.

This partial work is focused on ICP-MS techniques adapted to work with low volume samples. The main aim was to build up a technique to be able to handle low volume samples using oaTOF-ICP-MS. It was also necessary to characterize the system and to develop, optimize and validate a method for analysis of low volume environmental samples.

3.3.2 Results and discussions

This work proposed a suitable connection design of oaTOF-ICP-MS and a linear (syringe) pump for low volume sample analysis. Our unique arrangement has been characterized with respect to different introduction methods, sample consumption and other parameters. The introduction system consisted of a programmable linear pump, glass syringe with a 100 μL teflon capillary, Micromist nebulizer (400 $\mu L.min^{-1}$), and a two-shell thermostatic cyclonic spray chamber. The entire introduction system was connected to a conventional plasma torch and oaTOF-ICP-MS device (Optimass 8000, GBC). This arrangement was tested in both the continuous and discrete (fast injection

of defined volume of sample) sample introduction mode. With regards to the test results of both modes, it has been found that the discrete mode yields better results. Validation of the discrete method was done by analysis of different certified reference materials (water, hair, algae).

- **Continuous sample introduction mode with syringe pump**

The first experiment carried out in this work was dedicated to the continuous sample introduction mode with syringe pump and oaTOF-ICP-MS. The uranium standard of 1 $\mu g.L^{-1}$ was introduced into a mass spectrometer at various flow rates (5, 10, 25, 50, 75, 100, 200 and 300 $\mu L.min^{-1}$). Measurements were made in three replicates, with a total signal integration time of 5 seconds. The time required to stabilize the signal was found using the Time Scan software tool. The total time required for analysis, consisted of the transport time and the time needed to stabilize and integrate the signal. The signal intensity, resolution, signal stabilization time, total analysis time, total sample volume and RSDs were recorded for individual flow rates. Detection limits were calculated based on a 3 σ concept for the first calibration standard.

Flow rate [$\mu L.min^{-1}$]	Signal stabilization time [s]	Total analysis time [s]	Total sample volume [µL]	Signal intensity [counts]	Resolution	RSD [%]	Detection limits [$ng.L^{-1}$]
5	10	25	2	750	930	11,8	205
10	10	25	4	1750	1000	0,79	86,7
25	8	23	11	4500	1200	0,76	32,6
50	6	21	20	9000	1300	3,41	16,3
75	6	21	30	15000	1500	1,37	10,6
100	5	20	47	22500	1800	1,57	9,1
200	5	20	78	37500	1750	1,34	4,55
300	5	20	119	55350	2050	3,82	3,83

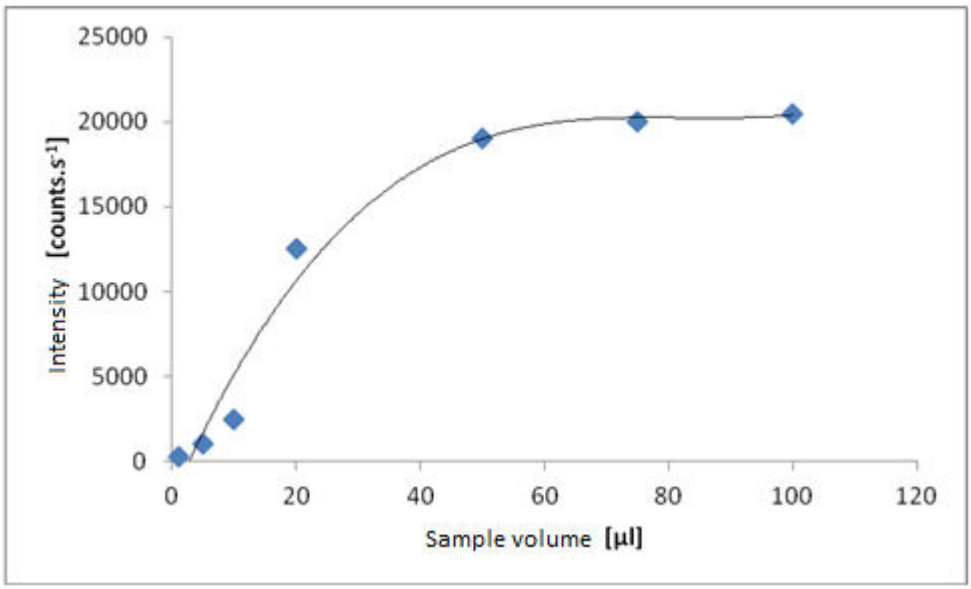
Table 3.: Characteristics for continuous introduction of sample by linear syringe pump (1 $\mu g.L^{-1}$, U^{238})

From the measured values it is clear see that the flow rate is a crucial parameter influencing the analytical performance of the technique.

- **Discrete sample introduction mode with syringe pump**

In addition to the continuous mode of sample introduction by linear pump, the discrete injection mode was used in this work. In the first phase, it was necessary to suck a certain amount of air into the teflon capillary. Further, a sample of the required

volume was taken behind this air plug and finally another air plug was formed in front. In a well-characterized teflon capillary (with respect to the internal volume) a separated zone of precisely defined sample volume was created. The prepared zone has prevented the sample being taken too early due to the self-aspirating effect of the nebulizer. The volume of both air "plugs" was typically around 100 µL. The advantage of such an introduction mode is the very precisely defined volume, which is injected into the system in a short time. Other advantages are higher intensities, better detection limits and shorter washing times in comparison to the continuous mode with linear syringe pump. The following graph shows the dependence of maximum U^{238} signal intensity on a sample volume. Sample flow rate = 800 µL.min^{-1}, U^{238}, 1 µg.L^{-1} (1, 5, 10, 20, 50, 75, 100 µL).



Graph 1.: Dependence of the signal intensity (U^{238}, 1 µg.L^{-1}, sample flow rate = 800 µL.min^{-1}) on the introduced sample volume

The best approach to discretely introducing the samples was found to be introduction of 50 µL at a sample flow rate = 800 µL.min^{-1}. Such a method for low volume samples was validated by analysis of different environmental certified reference materials (water, hair, algae). The memory effect and comparison with the regular peristaltic pump were also discussed in the submitted work.

4 Conclusion

The presented dissertation deals with the analysis of environmental samples using inductively coupled plasma mass spectrometry with orthogonal acceleration of ions and time-of-flight analyzer. At the beginning of the work an overview about mass spectrometry techniques used for elemental analysis is presented. Special focus is given on coupling of ICP and time-of-flight analyzers. The oaTOF-ICP-MS technique is a specific type of mass spectrometry. The separation of individual ions (isotopes) according to their m/z ratio is done by different time of flight. After the orthogonal acceleration pulse the lighter ions travel faster than the heavier ones and reach the detector earlier.

The GBC mass spectrometer used is capable of acquiring 30,000 full mass spectra in 1s. High speed can be advantageously used, for example, when a large number of isotopes in small volume samples needs to be analyzed. The entire mass spectrum is recorded very quickly without loss of sensitivity and regardless of the number of elements and isotopes determined. Due to these features the sample consumption is also very low. Low sample consumption is an advantage when a limited amount of samples is available or there is a need to eliminate the liquid waste as much as possible (analysis of radioactive and toxic substances). Due to high measurement speed, the technique also enables a higher rate of spectra acquisition than ICP ion source signal fluctuation. This velocity ensures high accuracy of isotopic ratios measurements. In the case when slower quadrupole mass spectrometers are used for isotopic ratios measurements, the signal fluctuation (plasma instability, introduction system instability, and other non-spectral interferences) may severely influence the quality of acquired data. Accurate measurement of a wide range of isotopic ratios (isotopic fingerprint) is essential for provincial and biomonitoring studies, where statistical data processing is further utilized. High speed data acquisition of full mass spectra is also very important for processing of transient signals (LA, ETV, etc.). Last but not least, the speed of analysis undoubtedly saves time. This dissertation discusses three different applications of oaTOF-ICP-MS for analysis of environmental samples.

The first application part deals with the use of oaTOF-ICP-MS for multi-elemental analysis of horse hair. A method for collection, pretreatment and analysis of these samples has been successfully designed in this section. Many authors have dealt with elemental composition of hair in terms of color, disease and other characteristics of horses. A large number of horse hair samples originated across the Czech Republic were analyzed. Results of the multi-elemental analysis were submitted for statistical data processing, which is not part of this work. Stabling, horse color, sex, and others have been used as factors that could affect the elemental composition of hair. However, the correlation of these factors with the elemental composition of the samples has not been demonstrated. The proposed oaTOF-ICP-MS method has achieved excellent analytical characteristics and has provided a high quality and fast multi-elemental analysis with preserved isotopic ratios for possible statistical investigations. A major challenge, however, was the method of pre-treatment of the horse hair samples. In order to obtain analytical information regarding the actual composition of the horse hair tissue it was necessary to separate endogenous and

exogenous contamination. Exogenous contamination consisted of dust, dirt, grease, etc., and had to be removed by an appropriate washing procedure. However, the washing procedure must not be too strong which could interfere with the internal structure of the hair. At the same time, it must be sufficient enough to remove the exogenous contaminants. Even the choice of the washing process itself, proved to be problematic. The best washing procedure was finally selected based on the analysis of washing solutions and washed trial samples. The chosen washing procedure showed the highest reproducibility and lowest RSD on five replicates of the trial sample. This finding, led to the hypothesis about non-affected isotopic ratios. Washed samples provided preserved isotope ratios. For this reason the samples were still suitable for statistical processing and the determination of whether any of the observed variables correlate with the elemental composition of the horse hair.

The second part of this dissertation was the analysis of carrots cultivated in different ways. The aim of this work was to compare three different growing systems (conventional production, "bio" production and production of small-domestic growers) with regard to the chemical composition of carrots. In the first stage, a large number of carrot samples were obtained. 76 samples of carrots came from small growers across the Czech Republic (domestic production). 71 samples were purchased at various shops and supermarkets. This group of samples was labeled as conventional, and commonly available. Additionally, 71 samples of carrots with the trademark "bio" were purchased. These 218 samples were subjected to a developed and optimized ICP-OES and oaTOF-ICP-MS analysis. The obtained results were compared with the available literature and valid legislation, and used for multi-criteria statistical evaluation of the quality of individual growing systems with respect to elemental composition (18 elements), nitrate and dry matter content. Time-of-flight mass spectrometry has proven to be a very valuable tool in terms of time savings, multi-elemental analysis, sensitivity and preservation of isotopic ratios. Unfortunately, subsequent statistical evaluation of the data did not reveal any correlation between the tested parameters and growing systems. Individual growing systems were not clearly divided on the basis of the elemental composition and the content of nitrates or dry matter. From this point of view, one cannot say whether "bio" production is better than other cultivation methods. The results obtained were compared with valid legislation. In all types of growing systems several samples with exceeded limit values for different contaminants were found. The most extreme values represented small-domestic growers. Rather than cultivation method used, the location and the quality of soil played important role in this case. A sample with the highest contamination was found to have originated from a field that was located on a former landfill site. Domestic growers may simply underestimate the quality of the cultivated land, which can be heavily contaminated, and this will then be reflected in the quality of the resulting crop. Regardless of the growing system used, carrots appeared as a very good nutritional source of potassium, magnesium, calcium, phosphorus, copper, manganese and zinc. When comparing with RDI, these nutrients have been found to have tens of percent RDI when consuming the average daily amount of carrots.

The last part of this dissertation deals with systems for introduction of small samples (especially low volume samples) into ICP techniques. In this work we also designed, optimized and connected such a system with oaTOF-ICP-MS. High

efficiency of sample transfer into ICP, low sample consumption and elimination of waste are the three main advantages of low volume sample introduction systems. Sample consumption may be a major problem if multi-elemental analysis of a limited quantity of sample is required. The combination of an efficient introduction system and a very fast simultaneous spectrometer makes oaTOF-ICP-MS a unique tool to analyse low volume samples. In our study, we replaced a classical peristaltic pump, from the introduction system, with a programmable linear pump. In comparison with the peristaltic pump, the linear pump represents a continuous flow even at low speeds and precise introduction management. In low flow rates a classical system with peristaltic pump, is influenced by serious fluctuation due to a peristaltic movement of tubing. The proposed linear pump system was compared with the conventional peristaltic pump system. The linear pump was tested in both the continuous introduction mode and the discrete mode, when a defined amount of sample was injected into the ICP. Detection limits, memory effects, sample consumption, etc., were investigated. We found the system with a linear introduction pump in discrete mode, to be most suitable to handle low volume samples. The best results were achieved for a short rapid injection of the 50 μL of sample at a rate of 800 $\mu L.min^{-1}$ into an introduction system (concentric Micromist nebulizer - cyclonic spray chamber – ICP). When compared to a classic arrangement with a peristaltic pump, the proposed technique was far more successful for working with low volume samples. The conventional layout under standard conditions required a sample volume of about 0.5 ml. The linear pump arrangement has been able to work fairly efficiently with samples of several tens of micro liters. The proposed unique linear pump introduction system coupled with the oaTOF-ICP-MS was validated by analyzing different environmental reference materials (water, algae and hair). Exceptional features of the oaTOF-ICP-MS, in combination with the linear introduction pump system, proved to be a very powerful tool in analyzing low volume samples. Time-of-flight mass spectrometry is a very useful technique for its multi-elemental capability, speed and simultaneity. These features are of great value for environmental samples. Very precise isotopic ratios obtained from such analysis can be used for large-scale statistical studies. The number of elements to be determined and their isotopes does not affect the accuracy, sensitivity or time required for analysis. Extensive sets of samples, where wide range of isotopes are needed to be determined, can be processed very quickly. With a modified time-of-flight mass spectrometry technique (proposed in this work), samples of micro litres can be analyzed irrespective of the number of elements and their isotopes.

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