# DEVELOPEMENT OF HIGH EFFICIENCY SAMPLE INTRODUCTION METHODS FOR ELEMENTAL ANALISYS

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PhD thesis summary and statements

Corvinus University of Budapest
Department of Applied Chemistry
Budapest, 2006

**PhD program**

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**Discipline**: Food Sciences

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**The approving signature of the Head of the Doctoral School and the Supervisor:**

The candidate has met all the requirements determined in the Doctoral Code Book of the Corvinus University of Budapest. He took the observations and suggestions arising during preliminary examination when reworking this dissertation, thus the dissertation can be put to public defense.

..... .....
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**The Local Doctoral Council for Life science of the Corvinus University of Budapest has been assigned in the resolution 3/10/2006 the following Thesis Committee for the public defense.**

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# 1 Introduction

"*There is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone. The rub comes in because elements never occur alone for both man and nature frown on celibacy.*" wrote G. E. F. Lundell a well recognized inorganic chemist of the first third of the 20th century in one of his publication from 1933. How is it all related to sample introduction and to the development of sample introduction techniques? If one considers, whether there is an elemental analytical task at all in which the sample can be analyzed without performing any preliminary changes on it, the conclusion might be that the only exception to Lundell's rule is when analyzing an atomic form of an element (e.g. mercury) in an inert gas mixture. In any other cases some kind of sample pretreatment or at least sample introduction resulting in the modification of the analyte in the sample must be carried out. IN ATOMIC SPECTROMETRY – EITHER IN THE CASE OF TECHNIQUES BASED ON THE ANALYSIS OF A RADIATION OR MASS SPECTRUM – THE ANALYTE MUST FIRST BE BROUGHT INTO THE FORM OF A GASEOUS, FREE ATOM.

In some types of elemental analysis the sample pretreatment steps can be eliminated (e.g. direct analysis of solid samples), nevertheless modifications of the analyte as a result of the sample introduction itself cannot be avoided (e.g. electrothermal vaporization or laser ablation). In the case of most sample types performing some kind of sample pretreatment is necessary. The primary reason for this that standards suitable for solid sample introduction methods (i.e., stable, homogenous) do not exist for every analytical tasks (e.g., food analysis), moreover in most of the times the sample itself does not meet these requirements either. Thus, most often the elements of interest are (i) extracted from a definite portion of sample devoted for analysis, (ii) this portion of sample is dissolved (acidic digestion, alkaline fusion) or (iii) combusted. After all these steps, there are countless methods available for introducing the analytes of interest into the source. These methods involving for example the following procedures:

- nebulization,
- derivatization,
- direct volatilization.

In order to find the best solution for sample introduction the type and amount of sample, analyte concentration and instrumentation availability should all be taken into account. Considering all of these – with reference to Einstein's relevant saying – the simplest possible method should be chosen, but not simpler.

In those cases when:

- only a small amount of sample is available,
- it has a complex matrix,
- contains the analytes of interest only in low concentrations,

or any possible combination of the above mentioned ones, the sample introduction methods conventionally used with elemental analytical methods are cannot in all cases be considered to be the most suitable ones. In this context, the followings are meant by generally or in other words conventionally used methods. The sample intended for elemental analysis generally appears as a solution that was prepared using some drastic digestion method. Optionally followed by some other procedures (evaporation, dilution etc.) this solution is most of the times introduced into the instrument by the means of pneumatic nebulization.

The application of this method – especially under the conditions mentioned above – means that **sample introduction might be the step restricting the performance of the entire measurement system. In most cases this issue originates from the insufficient introduction efficiency of the analytes of interest.**

That is the reason why, Browner and Broon has designated sample introduction as the Achilles' heel of atomic spectroscopy in a 1984 paper in *Analytical Chemistry*. Sample introduction efficiencies that can be achieved by the generally used pneumatic nebulizers are about of a few percentages, therefore the majority of the sample goes to waste. The above-cited authors said the followings about this subject: "*One of the most attractive aspects of liquid sample introduction is its relative simplicity and reliability. This allied with the fact that a sample dissolution step is often necessary to provide suitable sampling statistics, is probably the reason for the overwhelming use of liquid sample introduction in all branches of atomic spectroscopy. Nevertheless, a spectroscopist observing 99% of a hard won analyte solution going to waste is aware of the need for improvement*."

Despite of the above outlined features this sample introduction technique (i.e., pneumatic nebulization) can be considered the most widespeadly used one in atomic spectrometry, moreover in some cases it is assigned to be exclusive when illustrating this subject. With this end in view it does not necessarily mean it is perfect from all aspects.

## 2 Objectives

The aim of this work was to develop elemental analytical methods applying high efficiency sample introduction techniques instead of the conventionally preferred ones in this field. In my

opinion by focusing on the development of the sample introduction part of an analytical system one can find a relatively cost-saving way to create methods capable to effectively reduce the problems relating to conventional sample introduction systems and originating from the concomitant information loss.

One of the techniques popularly used for improving the efficiency of sample introduction is: gas phase introduction. Applying this procedure sample introduction efficiency can be improved even by two orders of magnitude, since a gaseous phase sample can practically be introduced in 100% into the analytical instrument. For the implementation of such a method the sodium-tetrahydroborate method is a widespreadly used derivatization technique. In the first part of my work I supposed to develop a relatively scarce multielemental method based on this technique.

The objectives of this experiment were the followings:

- **Development of a flow injection method suitable for measuring low volume samples**
- **Laying special emphasis on solving the problem relating to the simultaneous quantification of various analytes (species) having different propensities to hydride generation.**

In the next part of the work I supposed to develop a multielemental, flow injection sample introduction system, which is more universal than hydride generation, nevertheless still can be labeled as a high efficiency method. In this case sample introduction was carried out using a hydraulic high pressure nebulizer (HHPN). This technique is capable to produce much higher aerosol yield than most conventionally used pneumatic nebulizer.

The objectives of this experiment were the followings:

- **Optimization of the multielemental FI-HHPN-ICPMS system**
- **Characterization of the method when using for the analysis of low volume biological samples**

In the third part of my work, I investigated the feasibility of a multiply coupled SPME-GC-ICPMS system again applying the gas phase sample introduction technique for the determination of chromium in seawater.

The objectives of this experiment were the followings:

- **Development of an aqueous phase derivatization method enabling the use of gas phase sample introduction in as SPME-GC-ICPMS system.**

- **Applying the method for the analysis of real world samples.**

By fulfilling the above described objectives the bunch of usable analytical methods for the reliable determination of trace elements in low volume biological/environmental samples with complex matrices can hopefully be somewhat expanded.

# 3 Materials and methods

*The following reagents were used in the experiments:*

The digestion of samples were carried out using a mixture of nitric acid and hydrogen-peroxide. For calibration purposes multi element solutions made of single the element solutions of Ag, As, Ba, Cd, Co, Cr, Cu, Ga, In, Li, Mn, Mo, Pb, Sb, Se, Sn, Sr, Tl, V, and Zn were used along with $^{53}Cr$ enriched chromium standard solution. For hydride generation sodium tetrahydroborate stabilized in sodium hydroxide solution was used. Pre-reduction was performed with potassium iodide and ascorbic acid using hydrochloric acid to provide sufficient acidity. In the case of chelation derivatization: 1,1,1-trifluoro-2,4-pentandione was used as a chelating agent and methanol was necessary for its dissolution. Puffer solutions of the same method were made of sodium acetate, acetic acid and ammonia. The reduction of chromium was carried out by sulfur dioxide absorbed in water. In the case of gas chromatographic experiments toluene and crystalline chromium-tris(trifluoro-acetyl-acetonate) were used. Validation was performed by measuring the following reference materials: NIST 1643d (surface freshwater), PACS-2 (marine sediment), TORT-2 (lobster hepatopancreas), BCR 422 (cod muscle), IAEA MA-B-3/TM (fish homogenate), CASS-4 (near shore seawater).

*Used instrumentation:*

ICP-TOFMS, ICP-QMS, ICP-SFMS, GC-ECD, GC-QMS, HHPN, HPLC pump, SPME.

# 4 Results

## 4.1 Multielemental, flow injection ICP-MS method based on hydride generation.

First, the optimization of the ICP-TOFMS instrument parameters was carried out using continuous (stationer) hydride generation. Concentrations and flow rates of the hydride generation reagents were not optimized, these were adopted from literature in which similar set up was used. During the optimization it was established that changes in the flushing gas flow rate had the most significant influence on signal intensity. This can be explained by its multiple functions. On the one hand as a flushing gas its flow rate controls the separation of the volatile hydrides in the gas-liquid separator, while on the other hand as a carrier gas its flow rate should meet the requirements of the plasma.

After the optimization of the instrument parameters the length of the reaction tube serving as contact space for hydride generation reaction was optimized. By increasing the length of the tube the time the components spend in contact will also increase, but after a certain length intensities are decreasing. Hence, hydride generation reaction in the PTFE tube has a length (time) optimum. Following this phase of optimization the continuous sample introduction system was replaced with a flow injection one.

To handle the problem related to the different propensity towards hydride generation of the individual species the followings were done. Both analyte species in the sample and in the solutions prepared for calibration were uniformized by a chemical pre-reduction treatment (KI-ascorbic acid-HCl) prior to hydride generation. This means that elements in the sample and in the standard solution have been converted to the same oxidation state. With this method correct calibration could be obtained even if in the species pattern of the sample was to some extent different from the one in the standard solution.

The presented method has successfully been applied for the simultaneous determination of Ge, As, Sb, Sn, and Bi in the ng/ml ranges. The validation of the method was carried out for all analytes mentioned above (except Ge) by analyzing two different certified reference materials (NIST 1643d and PACS-2). It has been shown that the applied pre-reduction treatment enables to carry out accurate measurements in spite of the fact that the abundance of different species (with different oxidation states) in the sample and in the standard solution is not necessarily the same. Because of the additional uncertainty sources provided by the required treatment, the limits of detection became poorer, nevertheless it was only measuring with prior treatment that enabled us to achieve reliable results for both digested and not digested samples. Consequently it can be said

that the developed method successfully incorporates hydride generation as a high efficiency sample introduction technique and can both handle the problems arising when a multielemental hydride generation method is targeted. Due to the compromising pre-reduction treatment selenium should be eliminated from the set of analytes.

## 4.2 Hydraulic high-pressure nebulization sample introduction assisted multielemental, flow injection ICP-MS method.

Besides the advantages of the previously presented FI-HG-ICP-TOFMS method based on hydride generation, thus applying gas phase sample introduction some disadvantages have also arisen during the everyday routine use. The most important one among these is that the range of analytes is limited as evidently is for most methods applying a derivatization technique. In the case of this particular method, since the compromises needed due to multielemental characteristics the fall out of selenium has more reduced this range. Demand has arisen during everyday work for a method suitable for the determination not only of the hydride forming elements but several other ones in various biological and environmental samples.

Considering all of these, the more universal nebulization sample introduction was planned to be used with this method. In order to fulfill the needed detection limit requirements a high efficiency nebulizer was necessary. Hence, for sample introduction the hydraulic high-pressure nebulization was chosen. However, the flow injection method was kept since in the case of biological samples (i) the amount of sample is often limited, (ii) moreover memory effects (iii) and analysis time can be reduced.

The presented method has successfully been applied for the simultaneous determination of Ag, As, Ba, Bi, Cd, Co, Cu, Ga, In, Li, Mn, Mo, Pb, Sb, Se, Sn, Sr, Tl, V, and Zn. By using the flow injection sample introduction technique even 19 elements can be analyzed within 1 minute. The method requires only 200 μl of sample digest. Despite the extended glass surfaces in the sample introduction system (glass tubes in desolvation unit etc.) measurements can be carried out without any memory. No considerable matrix effects were observed when using this method; therefore quantification by external calibration can be applied. Due to the small consumed amount of sample the loading of the cones and the detector of the ICP-MS can be reduced. With the optimized parameters (instrument parameters, sample flow rate, aerosol carrier gas, desolvation) the method is proved to be suitable for the multelemental analysis of animal tissues with complex matrices. Accurately measured concentrations with the exception of Mo, Mn and As were presented for all reference values of the investigated CRMs.

## 4.3 Elemental analytical application of a chelation derivatization based SPME method for the determination of chromium.

The widespread use of ICP-MS has somewhat reduced the problems related to elemental analytical measurements (detection limits etc.), nevertheless several other problems have meanwhile appeared. Generally, when measuring an isotope below m/z 80 it can be said that one should surely count on some kind of interference. These interferences are more pronounced when measuring samples with complex matrices and moreover in the case of concomitant low analyte concentration. During my work both of these problems have occurred connecting to a real analytical task. In this chapter the summary of the method intended to cope with these problems is given.

I intended to implement the task focusing again on sample introduction, hence the feasibility of the followings were investigated. With derivatization followed by gas phase sample introduction analytes can be separated from the sample matrix, thus matrix related interferences can be reduced, moreover high salt content sample does not reach the source. The problem of low concentrations can be cured by applying pre-concentration.

For derivatization the β-diketonate chelating reagent (1,1,1-trifluoro-2,4-pentándion) well known for long in inorganic gas chromatography was chosen. During my work I was searching for the answer to the question whether SPME as an integrated extraction, pre-concentration and sample introduction technique is suitable for the above described sample introduction system and if yes, under what circumstances and how it can be harmonized with ICP-MS.

Prior to the development of the ICP-MS method with SPME sample introduction the flow of the different procedures of the method development along with their order had to be defined. The reason of this can be summarized as follows. In the case of methods with the type of sample introduction described above the analyte reaches the spectrometric source after (i) derivatization followed by (ii) an extraction step and finally (iii) going through a chromatographic system. It means that the only way to get any signal at the end is when derivatization, extraction and chromatography all work correctly. The individual optimization of every single part (unit) can only be performed however, if the entire measurement system works with parameters that are capable to provide reliable signals.

Following the elaborated method development procedures, the developed and optimized method has been proved to be suitable for the determination of dissolved chromium after derivatization followed by high efficiency gas phase sample introduction. The aim of the developed single phase derivatization procedure was to generate the Cr-tris[1,1,1-trifluoro-2,4-pentandione] complex of the water dissolved Cr(III) after reacting with the chelation reagent. This

complex is extractable by SPME, thus can be separated from the matrix and is suitable for the gas phase introduction of the analyte into the spectrometric source. Following these procedures the presented SPME-GC-ICP-MS system was successfully applied for the reliable determination of ultra trace levels of chromium in real world samples.

Finally, it can be added as a remark that the theory lying behind the procedures applied in this method is basically not element specific. Thus, the above presented method can be expanded to the analysis of other analytes which are – still with the most up to date instrumentation (e.g. ICP-MS) – challenging to determine, even if the concentration is low and the matrix is complex. However, going the sample preparation procedures somewhat more complex when using this method (derivatization, extraction) on the other hand a high sensitivity method capable of solving such special tasks as the investigation of environmental background values in the ultra trace range is received.

# 5 Thesis Statements

**1. I assembled a simultaneous, multielemental, flow injection inductively coupled mass spectrometric coupled system applying hydride generation sample introduction.**

On which I proved that:

a) In the case of a hydride generation based gas phase sample introduction technique, hydride generation reaction taking place in a capillary PTFE tube has its time (length) optimum.

b) When transient sample introduction is applied the shape of the signal peak (i.e., height/width ratio) alike the number of points available for drawing the envelope curve can be controlled by the variation of flow rate of the carrier stream.

c) In the course of multielemental analysis due to the applied KI-ascorbic acid pre-reduction treatment selenium has converted into its elemental form and consequently precipitated from the solution. Elemental precipitation may cause significant negative quantification error when a hydride generation based gas phase sample introduction method is applied or in extreme cases thus the given compound cannot be analyzed. Nevertheless, in the case of other elements (As, Sb, Ge, Bi, and Sn) the same treatment resulted in improved precision for the same solutions.

**2. I assembled a multielemental, flow injection, hydraulic high pressure nebulization-inductively coupled mass spectrometric coupled system suitable for the analysis of biological samples.**

On which I proved that:

a) When using a hydraulic high pressure nebulizer (HHPN) the solvent loading on the plasma is significantly increasing and thus, the exciting-ionizing capability of the plasma is deteriorating. Therefore, more not dissociated oxide ions gets into the mass spectrometer from the plasma. This analytically multiply disadvantageous phenomenon can effectively be reduced by performing high tempereture (150-170 °C) desolvation after nebulization. I proved that in the case of mass spectrometric (MS) detection the optimization of the (heating and cooling) temperatures of desolvation can be implemented by monitoring the CeO/Ce mass ratio.

b) In the case of an elemental analytical method with element selective detection the acid content of the introduced sample can dissolute troublesome amounts of Cu, Mn, Mo

(depending on the material of the parts) from the metal parts of the sample introduction system even during a residence time of a couple of tens of seconds typical for transient sample introduction techniques.

c) With the use of the hydraulic high pressure nebulizer (HHPN) in association with a flow injection introduction technique it is possible to analyze the trace element content of very low volume biological samples.

**3. I elaborated a flow of method development procedures applicable in the case of gas chromatographic spectrometric methods using batch derivatization and extraction.**

On the grounds of a real application of the methodology I proved that:

It is suitable for the individual optimization of a given unit (derivatization, extraction etc.) of the analytical system. The entire analytical system will work under optimal conditions followed by this unit-by-unit optimization.

**4. By developing an aqueous phase derivatization procedure based on chelation reaction I implemented the quantitative extraction of Cr(III) from aqueous solution using the solid phase microextraction (SPME) technique.**

On which I proved that:

a) The quantitatively generated Cr-tris[1,1,1-trifluoro-2,4-pentandione] complex, or Cr-trifluoro-acetyl-acetonate abbreviated as $Cr(TFA)_3$ is suitable (inert, sable) for capillary gas chromatography.

b) The time requirement of the chelation reaction between Cr(III) and 1,1,1-trifluoro-2,4-pentandione in a (single) aqueous phase medium is significantly lower than the one under similar conditions but in a two phase (organic solvent-water) system, because the metal ions and the non-polar chelation reagent both dissolved in the aqueous phase do not have to cross a phase boundary during the reaction.

c) The solid phase microextraction of the $Cr(TFA)_3$ complex with poly-dimethylsiloxane sorbent cannot reach equilibrium even during long extraction times (i.e., few hours) when the immersion technique is used under conditions that according to the literature are considered general (ambient temperature stirring, sorbent volume of a couple of tens of microliters).

d) In the case of Cr(III) analysis in the form of $Cr(TFA)_3$ complex applying solid phase microextraction-gas chromatographic (SPME-GC) sample introduction and inductively coupled plasma-mass spectrometric (ICP-MS) detection no mass spectrometric interferences (e.g., $ArC^+$) were observed at values of m/z = 52 and 53 even when a gas chromatographic system resulting only in negligible separation capability was used.

# 6 Publications

*In journals with impact factor.*

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| 2003 | **L. Abrankó**, Zs. Stefánka, P. Fodor, Possibilities and limits of the simultaneous determination of As, Bi, Ge, Sb, Se, and Sn by flow injection–hydride generation–inductively coupled plasma–time-of-flight mass spectrometry (FI–HG–ICP–TOFMS), *Analytica Chimica Acta* **493** (2003) 13-21., **(2003 ISI- impact factor: 2.210)** |
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*In journals without impact factor*

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Rak G., Béres I., Bognár Á., **Abrankó L**., Fodor P., Borok Pb-izotóp arányainak mérése ICP-TOFMS technikával, Lippay János - Ormos Imre – Vas Károly Tudományos Ülésszak (Budapest) 2005. október 19-21.

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*International abstract*

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| 2003 | **L. Abrankó**, Zs. Stefánka, E. Kápolna, P. Fodor, *Flow Injection ICP Time-of-Flight Mass Spectrometry Coupled to Hydraulic High Pressure Nebulizer for the Analysis of Low Volume Biological Samples*, 2003 European Winter Conference on Plasma Spectrochemistry (Garmisch-Partenkirchen), 2003. (poszter alapján) |
| 2004 | Cs. Sörös, **L. Abrankó**, M. Dernovics, M. Üveges, P. Fodor, *The role of As, Hg, Se, and Sn speciation in food analysis*, CE Food (Budapest) 2004 (poszter alapján) |
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| | **L. Abrankó**, Zs. Jókai, B. Kmellár, P. Fodor, *Method development for mercury speciation studies in fish samples intended for human consumption*. XII HUNGARIAN-ITALIAN SYMPOSIUM ON SPECTROCHEMISTRY ENVIRONMENTAL POLLUTION AND HUMAN HEALTH Pécs, 23 – 27 October 2005. (előadás alapján) |
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*Hungarian book, book section*

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