UNIVERSITY OF PARDUBICE

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Institute of Environmental and Chemical Engineering

Ing. Jan Patočka

The use of ICP-MS in the connection to ETV for analysis of environmental samples

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Author: **Ing. Jan Patočka**
Supervisor: **doc. Ing. Anna Krejčová, Ph.D.**
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Abstract

The first chapter of this dissertation is devoted to the literature research focused on ETV-ICP-MS. An overview of available ETV-ICP-MS instrumentation is given. The optimization of the ETV-ICP-MS working conditions and suitable calibration strategies are discussed.

In its practical part, the presented dissertation deals with the validation and testing of ETV-ICP-MS. This technique is used to analyse real environmental samples and samples of certified reference materials. The analytical performance of the ETV-ICP-MS method in the analysis of solutions and slurries is compared to the performance of a conventional ICP-MS method for solution analysis using a nebulizer and a spray chamber as the sample introduction system and to the performance of the SS-HR-CS-GFAAS technique adapted to analyze solid samples. The following part is devoted to the study of the analyte transport efficiency in ETV-ICP-MS, which is related to the use of chemical modifiers. The outcome of this study is the proposal and validation of the new analyte transport efficiency modifier for ETV-ICP-MS based on carbon microparticles acting as analyte carriers. The last part is devoted to a user evaluation of the ETV-ICP-o-TOF-MS instrumentation from GBC.

Abstrakt

První kapitola této disertační práce je věnována literární rešerši zaměřené na ETV-ICP-MS. Je zde diskutována instrumentace a optimalizace pracovních podmínek ETV-ICP-MS včetně volby vhodné kalibrační strategie.

Předložená disertační práce se ve své praktické části zabývá validací a testováním techniky ETV-ICP-MS. Tato technika je využita pro analýzu reálných vzorků životního prostředí a vzorků certifikovaných referenčních materiálů. Analytický výkon metody ETV-ICP-MS v analýze kapalných a suspenzních vzorků je porovnán s výkonem klasické ICP-MS roztokové analýzy s využitím zmlžovače a mlžné komory jako systému pro zavádění vzorku a s výkonem techniky SS-HR-CS-GFAAS uzpůsobené k analýze pevných vzorků. Následují část je věnována významu účinnosti transportu analytu v ETV-ICP-MS, s čímž souvisí použití chemických modifikátorů. Výstupem této studie je návrh a validace nového modifikátoru účinnosti transportu analytu pro ETV-ICP-MS, který je založený na uhlíkových mikročásticích, které fungují jako fyzické nosiče analytu. Závěrečná část je věnována uživatelskému zhodnocení instrumentace ETV-ICP-o-TOF-MS od firmy GBC.

Keywords

ETV-ICP-MS, Slurry analysis, Solution analysis, Thallium, Certified reference materials, Analyte transport efficiency, Carbon microparticles, Chemical modifiers

Klíčová slova

ETV-ICP-MS, analýza suspenzí, roztoková analýza, thallium, certifikované referenční materiály, účinnost transportu analytu, mikročástice uhlíku, chemické modifikátory

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0 Introduction

The combination of the detection power of the inductively coupled plasma mass spectrometry (ICP-MS) with the electrothermal vaporization (ETV) as a sample introduction system allows the analysis of complicated samples in liquid, slurry and solid form. A very small amount of sample (typically 5 – 40 μl) is sufficient for one analysis. The combination of those techniques improves even further the already very low limits of detection of the ICP-MS due to the higher analyte transport efficiency to the plasma provided by the ETV. The improvement of procedural detection limits is also associated with the ability to analyse less diluted samples. This instrumental connection was firstly published by C. J. Park in 1987 [1] as a response to problems associated with the classical sample introduction system realised by a nebulizer and a spray chamber. This sample introduction system suffers from a high spectral background due to the high water load into the plasma. The design of the ETV unit is most often based on the design of the electrothermal atomizer based on the principle of the resistively heated graphite furnace, which is used as an atomizer for the atomic absorption spectrometry (ETA-AAS) [2, 3].

The complicated and time demanding optimization of the ETV-ICP-MS working conditions did not allow the ETV to become a routine sample introduction system for the ICP-MS. The potential of the ETV for reducing polyatomic spectral interferences in the ICP-MS has been overcome by the arrival of mass spectrometers using the sector analyser that provides a high resolution sufficient enough to eliminate most spectral interferences, and also by the implementation of collision / reaction cells to the design of new quadrupole based instruments. Improved high efficiency nebulizers for analysis of small samples have also been available. Therefore, the systems allowing to dose small and discrete volume of sample, such as the flow injection analysis (FIA) could have been used. The analysis of slurry samples using the ICP-MS was also solved by new nebulizers of the Babington and Burgener design, which could be directly connected to the plasma torch for that purpose. Despite the ETV-ICP-MS had not been chosen as a routine sample introduction system, it still has its place in the analysis of complicated samples. Since the ETV-ICP-MS is not a routine analytical technique, its commercial availability is quite limited. Most of the instrumental connections used in available literature were homemade systems assembled from the ETV unit and the ICP-MS from different manufacturers. The ETV systems commercially available nowadays are ETV GF 5000 (GBC), ETV HGA 610 MS (Perkin Elmer) and ETV 4000C (Spectral Systems) [2, 4-6].

1 Theory

ETV instrumentation and operating

The electrothermal vaporizer can be made of graphite, tungsten, tantalum and rhenium. ETV devices can have a different construction. Most often it is a furnace and also a strip, a coil, a boat, a fibre or a platform placed in a furnace. The device, in which the electrothermal vaporization occurs, is connected to the plasma torch with a transport tube. The sample can be dosed using a micropipette or an autosampler. The development of ETV-ICP-MS eventually led to the use of a graphite furnace as a vaporizer, although the properties of some alternative vaporisers would be in some cases of greater benefit (e.g. analysis of carbide-forming elements that are getting embedded in the graphite furnace). The resistively heated graphite furnace has proven to be the best compromise solution to fully exploit the versatility of ETV as a sample introduction system. Most of the ETV units introducing samples into the ICP-MS are modifications of the graphite furnace atomizers used in the ETA-AAS. An important parameter of the ETV unit design is the carrier gas flow, which significantly affects the efficiency of analyte transport to the ICP. The pneumatically operated graphite probe is used to close the dosing orifice of the graphite furnace before the temperature program begins. The most commonly used commercially available electrothermal vaporization unit is the Perkin Elmer HGA-600MS unit [2, 7]. Other variations of the ETV unit design are often home-made systems where the vaporizer itself is located in a dome or a cylindrical chamber. The graphite rod or coil is enclosed in a quartz dome that is purged by a carrier gas stream (argon). The rod is usually 6 mm long and has a 1 mm deep notch where the sample is dispensed. An alternative to the rod may be a 20 mm long fibre. The carrier gas flows tangentially to prevent condensation on walls [8]. The use of a tungsten coil, which is enclosed in a cylindrical quartz chamber, is also described. The advantage of using a coil instead of a fibre is an extension of the active length of an atomizer in an equally sized chamber. Another advantage is the low cost and high reproducibility [3, 9].

The experiences from atomic absorption spectrometry with electrothermal atomization (ETA-AAS) can be utilised in the ETV only to some extent, because the main purpose of ETV and ETA is different. The goal of ETA is the formation of free atoms of analyte or their time separation from components of sample matrix that could cause analyte losses and problems at the background correction. The purpose of ETV is the rapid, efficient and stable transport of vaporized analyte to the ICP where the atomization and ionization take place [10]. The ICP-MS offers almost complete elemental and isotopic analysis for most samples over a wide range of concentrations. Although ICP-MS has become a very powerful analytical technique, there are some limitations. These limitations including mainly isobaric and polyatomic interference and sample matrix effects can be partly overcome by using the ETV as a source of analytes.

Using the electrothermal vaporization in the connection to the inductively coupled plasma mass spectrometry (ETV-ICP-MS), the sample is dosed to the graphite furnace by the autosampler. Then, the dosing orifice of the furnace is closed and the temperature program that is similar to one used in the ETA-AAS is employed. When estimating a temperature range for the optimization of the temperature programme, the knowledge of the boiling point of an analyte is usually used. Two different scenarios can occur in the relationship between an analyte and a sample matrix. The boiling point of an analyte may be either higher than the boiling point of a sample matrix, or vice versa. In the first case, the temperature programme aims to eliminate sample matrix components before the analyte is vaporized. In the case where the analyte is more volatile than sample matrix components, it is desirable to vaporize the analyte before them. In both cases, a common routine is the use of chemical modifiers. When using a graphite furnace as a vaporizer, the working temperature range is from room temperature up to 3000 °C and the maximum temperature rise rate is 2000 $°C\ s^{-1}$. The temperature stress of the graphite furnace at high temperatures has a significant effect on its lifespan. The ETV temperature programme can be divided into four basic steps, which may further include sub-steps [2]. The purpose of these steps is the vaporization of analyte and its transport into the ICP-MS by the sample gas flow [2, 11].

The development of ETV-ICP-MS method includes optimization of the ETV temperature programme along with the selection and further optimization of a modifier that can have various functions. The first step after dosing the sample is drying to evaporate the solvent. The temperature is chosen slightly above the boiling point of the solvent and its rise should not be too steep to avoid the risk of analyte loss. The next step is pyrolysis to remove the sample matrix without any analyte loss. The stability of analyte at higher temperatures during pyrolysis can be increased by using a chemical modifier. In the vaporization step, the analyte is rapidly vaporized. The fast temperature rise is used. The optimal duration of this temperature is one whose further extension no longer increases the signal intensity. Chemical modifiers can be used to reduce the optimum vaporization temperature for elements of a high boiling point to increase their volatility. The final step is cleaning, in which the temperature is higher than in the vaporization step to eliminate any analyte residues from the graphite furnace. A very rapid increase in temperature is used and the duration is optimized to achieve the lowest and constant blanks [2]. The optimization of the temperature of pyrolysis and vaporization step and its increase rate is achieved by measuring repeatedly a standard solution or a sample while gradually changing the working temperature. In the case of a more complicated sample analysis, it is possible to either omit the individual steps completely or use them multiple times even with the repeated dosing of a modifier.

Various substances and elements can serve as transport modifiers such as HCl, NH_4Cl, Pd, Rh, Ir, Au, Mg, ascorbic acid, citric acid, Triton X-100 and CCl_4 [2]. The CRM NASS-3 seawater can be used as a multicomponent physical carrier for analytes of a wide range of volatilities [12]. In the nineties of the last century, citric acid (CA) and other organic compounds were evaluated as transport modifiers [2]. Carbon particles produced from organic compounds during pyrolysis can serve as analyte condensation sites and then act as carriers, improving the analyte transport efficiency [13, 14]. However, the disadvantage of using organic compounds as a modifier could be the increased formation of carbon-containing molecular ions that interfere with light elements such are Mg, Si, Ti, Ca and Cr [14]. Carbon particles can be also produced from gaseous organic compounds as CCl_4 when it is added to the sample gas flow [2, 14].

Typically, the ETV-ICP-MS connection is made using a Teflon® or Tygon® tube of 50 - 70 cm in length and 6 mm inner diameter. The carrier gas flow is determined experimentally depending on the signal intensity [15]. The realization of the connection of the ETV unit and the ICP-MS was studied with a focus on the analyte transport efficiency [16]. The explanation of the processes taking place on the way from the ETV to the ICP was given by Kántor [17]: the aerosol generated in the ETV is successfully transported by the carrier gas if the formation of particles large enough takes place. On the other hand, generated particles have to be small enough to prevent their deposition on the way to the ICP. Furthermore, the analyte transport efficiency depends on the carrier gas flow conditions and the heating conditions in the graphite furnace. The faster heating rate leads to a higher analyte vapour concentration that results in an increasing self-nucleation. The transport efficiency also depends on analyte volatility and the type of sample matrix [2, 18]. The analyte loss on the way to the ICP is strongly dependent on the ETV unit design. As reported by Grégoire and Sturgeon [19] and Sparks et. al. [16], the major analyte loss varying between 70 % and 80 % takes place at the switching valve in the ETV unit.

2 Objectives of the dissertation

The aim of this dissertation is to evaluate the analytical possibilities of the ETV-ICP-o-TOF-MS instrumentation. The purpose of the literary part is to elaborate a review concerning ETV-ICP-MS and its applications. The practical part is divided into three objectives.

Objective 1: To compare the analytical performance of ETV-ICP-MS in the analysis of slurry and liquid samples with the competing techniques such as ICP-MS using a classic nebulizer and a spray chamber as the sample dosing system and with the solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry (SS-HR-CS-GFAAS). To include the time requirements of individual methods for sample preparation and also the overall time required for the analytical process from the original sample to its successful analysis. For this part of the study, to design a suitable analyte and a suitable type of sample to make this comparison.

Objective 2: To apply the experiences gained from Objective 1 for studying the possibilities of modifying the conditions of the analyte transport into the plasma to increase its efficiency. To focus on the use of substances (e.g. citric acid) that generate carbon particles in situ. To design a suitable modifier to improve the conditions for the analyte transport into the ICP-MS. To select suitable analytes that can be used to accomplish this goal.

Objective 3: To critically evaluate the instrumental connection of ETV-ICP-o-TOF-MS from GBC Company (Australia) based on user observations gained when working on Objectives 1 and 2. To discuss technical and software shortcomings of this instrumentation.

3 Experimental

3.1 Standard solution, reagents and samples

All reagents were of an analytical-reagent grade. 65% (v/v) HNO_3 (LachNer, the Czech Republic) was distilled in a sub-boiling distillation equipment (BSB 939 IR, Berghof, Germany). Deionised water was purified using the SG Ultra Clear system (SG Water, USA) and using the Milli-Q system (Millipore, USA) for SS-HR-CS-GFAAS. For an instrumental calibration and a sample spiking, commercially available single-element standard solutions Tl and Au 1.000 ± 0.002 g L^{-1} (Analytika Co. Ltd, the Czech Republic) were used. In 1.000 ± 0.002 g L^{-1} (Analytika Co. Ltd, the Czech Republic) was utilised as an internal standard for ICP-MS. Matrix modifiers palladium nitrate 20 g L^{-1} (SCP Science, Canada), citric acid monohydrate with a purity $\geq$ 99.9998% (Sigma Aldrich, Germany) and the physical carrier carbon microparticles (CMs) „RP07” (Synpo a.s., the Czech Republic) were used for the ETV-ICP-MS. For slurry preparation, Triton X-100 (Sigma Aldrich, Germany) was used. For methods validation, the CRMs GBW 10052 green tea, GBW 07601 human hair (both GBW, China), BCR 679 white cabbage (IRMM, Belgium) and EnviroMAT Drinking water (EP-H-2) (SCP Science, Canada) were used. Sample of spruce needles (SN-sample) was collected during spring 2015 in the city of Pardubice (the Czech Republic).

3.2 Instrumentation

Samples of needles were dried in the laboratory oven UM 400 (Memmert, Germany), milled in the Freezer/Mill 6970 (SPEX Sample Prep, USA) and digested using the Microwave system SpeedwaveTM MWS-2 with high-pressure PFA vessels DAC-70S (the maximal pressure 100 barr, the maximum total output of the microwave generator 1000 W; Berghof, Germany). The particle size of milled samples was determined using Mastersizer 2000 (Malvern Instruments, England). The field emission scanning electron microscope (FE-SEM) Lyra 3 (Tescan, the Czech Republic) was employed for CMs particle size determination. The FE-SEM scans were acquired at 10 kV acceleration voltage on 2.5, 5, 30 and 100 µm view field windows.

The inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometer (ICP-o-TOF-MS) Optimass 9500 (GBC Scientific Equipment, Australia) was equipped with the concentric nebulizer MicroMist (400 µL min^{-1}) and the 70mL thermostated (10 °C) cyclonic spray chamber (both Glass expansion, Australia) for solution nebulizing or coupled to the ETV unit GF 5000 (GBC Scientific Equipment, Australia). The transfer line between ETV and ICP-MS was ensured using the Tygon® tubing of the total length 100 cm and the inner diameter 4 mm. Classical pyro-coated graphite furnace tubes (GBC, Australia) were used for the ETV-ICP-MS analysis. The ETV unit was equipped with the PAL Auto Sampler 3000 (GBC, Australia). The quartz dosing capillary QC-3000-Kit (GBC, Australia) of the inner diameter 500 µm was used. The operating conditions of the ICP-MS analysis for the solution nebulization were adjusted to compromise the sensitivity and resolution of the instrument for ^{238}U as well as to obtain UO^+/U^+ ratio below 5 % (Table I). The sensitivity of 70000 counts s^{-1} and resolution of 2040 were reached for the isotope ^{238}U in the tuning solution containing 1 µg L^{-1} of U. The external aqueous calibration Tl solutions containing the internal standard In were used. The operating conditions of the ETV-ICP-MS analysis were set up in a similar way using a classical nebulizer and a spray chamber system as described above. However, in this case, the operating conditions markedly depended on the actual condition of the second skimmer cone, which deteriorated significantly faster in the connection to the ETV. The sensitivity for ^{238}U varied between 20000 – 50000 counts s^{-1} and resolution 1500 – 2000. Then the ETV unit was connected to the ICP-MS and operated under thus optimized working conditions.

The solid sampling high-resolution continuum source atomic absorption spectrometer with a graphite furnace atomizer ContrAA 700 (SS-HR-CS-GFAAS; Analytik Jena, Germany) was employed. The instrument is equipped with the xenon short-arc lamp (GLE, Germany) as a radiation source, the high-resolution double Echelle monochromator (DEMON), the linear CCD array detector with 588 pixels (200 of them for monitoring the analytical signal and performing background corrections, the remainder for correcting for fluctuations in the lamp intensity etc.), the transversely heated graphite tube atomizer and the automated solid sampling accessory (SSA 600) with an incorporated microbalance (a readability of 1 µg). Pyrolytic graphite tubes and solid sampling graphite platforms were utilised.

3.3 Sample preparation

Spruce needles were separated from twigs, cut into pieces about 1 – 2 mm, dried in the laboratory oven to the constant weigh and homogenised in the cryogenic mill in liquid nitrogen (the final volume diameter was about 15 µm). For the microwave decomposition, just about 0.3 g of powdered spruce needles or CRMs was inserted into the vessel together with 6 mL of distilled 65% HNO_3 and allowed to react in an open container for 10 min. Then, the three-steps decomposing programme was employed: (1) 160 °C, 5 min, 80% of power; (2) 200 °C, 10 min, 80% of power and (3) 10 min without heating. The final volume was 25 mL. Sample blanks were prepared together with the samples. The mineralised samples were analysed directly without any additional steps using ETV-ICP-MS. Before the ICP-MS analysis, the mineralised samples were diluted tenfold. At this dilution step, the internal standard In was added at the final concentration 0.5 µg L^{-1}. For the SS-HR-CS-GFAAS analysis, just about 1 mg of sample or CRMs was weighted directly on a graphite platform in the device.

For the preparation of slurries, just about 25 mg of powdered spruce needles or CRMs was transferred into a 5mL flask, 0.5 mL 1% Triton X-100 was added to achieve a homogenous and stable slurry, and the flask was made up with demineralised water. The slurries were dispersed in the ultrasonic bath for 20 min and shaken intensively just before analysis. Carbon microparticles were added directly into samples and calibration standard solutions during their preparation. With the use of CMs, every sample / standard solution was turned into a slurry made in 0.1% Triton X-100 and 0.65% HNO_3 (HNO_3 was not added into mineralized samples as they contained it already).

4 Results and discussion

4.1 A comparison of the analytical performance of spectrochemical methods

Four methods are employed for the determination of Tl in spruce needles: ICP-MS analysis of decomposed samples, ETV-ICP-MS analysis of decomposed and slurry samples and SS-HR-CS-GFAAS. The methods are compared in terms of the analytical performance and their practical laboratory aspects: difficulty of the preparation of samples for analysis, the method optimization and validation and the time consumption. The analytical performance is assessed regarding the analysis of trace heavy metals in the environment. Spruce needles were chosen as a sample in order to ensure reliable results from all four methods without unnecessary complications during sample preparation steps, e.g. a tiny, very resistant or extremely hard sample. Thallium was chosen as an analyte because it is considered an easy analytical task from the point of view of ICP-MS for no spectral interferences occurrence and a difficult analytical task for ETV. Therefore, all attention could be focused only on the ETV processes problematics.

4.1.1 Optimization and validation of the methods

The ETV temperature programme and the amount of modifier were optimized by the means of the repetitive analysis of a solution containing 0.5 μg L^{-1} Tl. The external aqueous calibration Tl standards and the mixed modifier $Pd(NO_3)_2$ with citric acid were used (4 μL dosed, it means 4 μg of $Pd(NO_3)_2$ and 500 μg of citric acid). The temperature programmes for digested and slurry samples (slurry sampling SlS-ETV-ICP-MS) were: the pyrolysis and vaporization temperatures 1000 and 1450 °C for solutions and 1000 °C and 1800 °C for slurries (Figure 1). The optimization of the modifier is shown in Figure 2. The working conditions for the SS-HR-CS-GFAAS were optimized similarly to the ETV-ICP-MS. The external aqueous calibration Tl solutions and the modifier 1 g L^{-1} of $Pd(NO_3)_2$ (10 μl dosed) were used. The pyrolysis and atomization temperatures were 1000 and 2000 °C (shown in Figure 1).

The validation of the method covered all steps involved in the analytical process, i.e. from preparation to analysis (procedural sample blanks, spiked samples, control standards and certified reference materials, if they are available). The recovery expressed as a ratio of measured and theoretical (or certified) concentration was assessed for: (i) the standard solution mineralised in the microwave oven (n=3, 0.1 μg L^{-1}), (ii) the SN-sample spiked with Tl before the decomposition step (n=3, the concentration of added Tl in the final solution 1 μg L^{-1}), and (iii) CRMs (GBW 10052 Green tea, BCR 679 White cabbage, EnviroMAT Drinking water EP-H-2; n=3). From Table 1, a very close approach of recoveries to the theoretical 100 % is evident for all items in the recovery study. Sample blanks prepared in each MW mineralisation run contained no detectable amount of Tl. Any losses and contaminations were not observed in the decomposition step.

The comparison of the used analytical methods in terms of their time demands of sample preparation, method development and overall demands is given in Table 2.

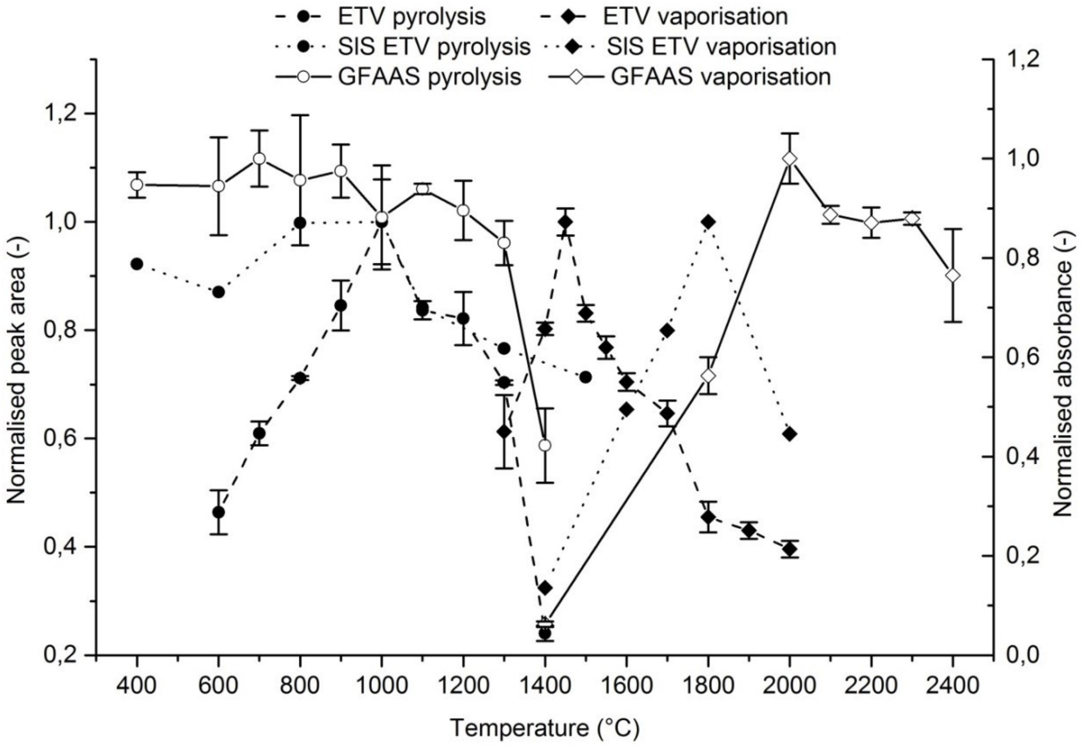

Figure 1: The optimization of the pyrolysis and vaporization / atomization temperatures

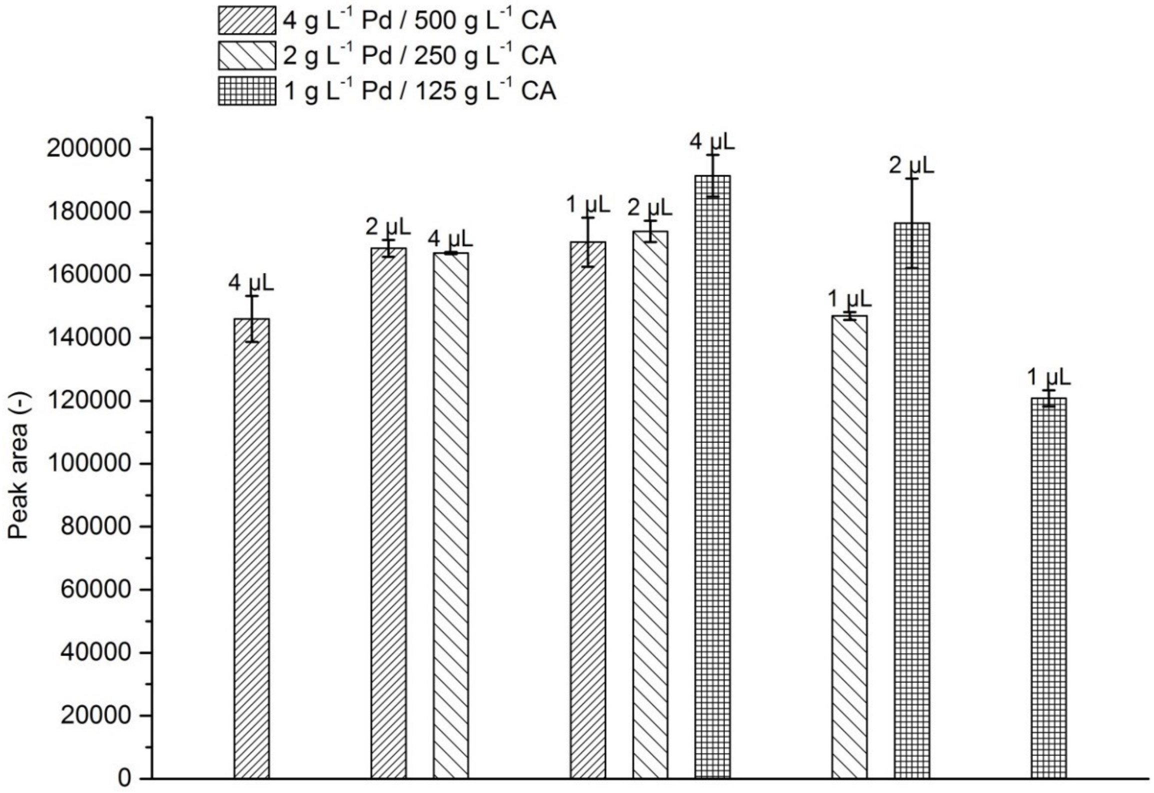

Figure 2: The optimization of modifier for the ETV-ICP-MS analysis

Table 1: Validation and analytical performance of the used methods in the analysis of Tl

			ICP-MS		ETV-ICP-MS		SlS-ETV-ICP-MS		SS-HR-CS-GFAAS	
Validated item	Tl standards / spikes		R, %	RSD, %	R, %	RSD, %	R, %	RSD, %	R, %	RSD, %
	Tl 0.01 μg L^{-1}		107	2.1						
	Tl 0.1 μg L^{-1}		107	2.4	114	19	94.5	2.2		
	Tl 1 μg L^{-1}		104	1.9						
	Tl 3 μg L^{-1}								124	3.3
	Tl 5 μg L^{-1}								111	2.3
	Tl 10 μg L^{-1}								103	0.17
	MW[a] Tl 0.1 μg L^{-1}		97.5	5.5						
	SN-sample + Tl 1 μg L^{-1}		91.6	5.8						
	CRMs	certified	found[b]							
	GBW 10052, μg kg^{-1}	57 ± 11	46.6 ± 1.7		46.3 ± 3.3					
	BCR 679, μg kg^{-1}	3 ± 0.3	3.3 ± 0.2		2.8 ± 0.1				3.05 ± 0.2	
	*Enviro*MAT, μg L^{-1}	0.0965 ± 0.0205	0.0861 ± 0.0130							
	SN-sample[c] μg kg^{-1}		10.5 ± 0.8		13.0 ± 1.2		12.3 ± 1.6		9.82 ± 1.2	
Analytical performance	LOD$_{\text{instrumental}}$, ng L^{-1}		0.22		0.12		0.12		1200	
	LOD$_{\text{procedural}}$, μg kg^{-1}		0.18		0.0099		0.024		1.2	
	LOD$_{\text{absolute}}$, pg		---		0.0024		0.0024		12	
	R[d], %		92–107		90–114		94.5–117		90–124	
	RSD[e], %		1.9–6.2		5.2–19		6.3–17		0.17–15	
	Calibration, correlation coefficient		0.9999		0.9993		0.9993		0.9988	

[a] Tl standard solution MW mineralised

[b] The results expressed as mean value ± standard deviation

[c] The SN-sample used as an auxiliary laboratory reference material

[d] The range of recoveries in the validation study

[e] The range of repeatabilities in the validation study

Table 2: The comparison of the time consumption, laboratory demands and overall difficulty of all methods

		ICP-MS	ETV-ICP-MS	SlS-ETV-ICP-MS	SS-HR-CS-GFAAS
Time requirements	Cutting + drying	1 day	1 day	1 day	1 day
	Grinding	(1 hour)	(1 hour)	1 hour	1 hour
	MW digestion	1 hour	1 hour	-	-
	Slurry preparation	-	-	15 min	-
	Sample dilution	10 min	-	-	-
	Analysis time of 1 sample series[a,b]	5 min	75 min	75 min	75 min
	Total time demands of 1 sample series[a,b]	135 min	195 min	150 min	135 min
Optimisation	Method optimization				
	Temperature programme optimization	no	yes	yes	yes
	Modifier optimization	no	yes	yes	yes
	Slurry preparation optimization	no	no	yes	no
	Sample particle size problems	no	no	yes	no
	Calibration against aqueous standards	yes	yes	yes	yes
	Use of internal standard	yes	no	no	no
Validation	Reference materials	yes	yes	-	yes
	Recovery	yes	yes	yes	yes
	Repeatability	yes	yes	yes	yes
	Mineralized spiked samples	yes	yes	no	no
Difficulty	Sample preparation[c]	4	3	2	1
	Method optimization[c]	1	3	4	2
	Method validation[c]	1	3	4	2
	Total difficulty of the method[c]	1	3	4	2

[a] Each sample series includes 3 samples and 2 blanks

[b] The number of each sample replicates was 2 for ETV-ICP-MS and 3 for ICP-MS and SS-HR-CS-GFAAS

[c] The grades (1 – 4) indicate the level of the procedure difficulty for each method

4.1.2 Summary for the goal 1

This work is focused on presenting of not only top analytical results but reveals other, sometimes from a practical perspective more important aspects of the analytical work, which are often hidden behind the great analytical performance. In the case of Tl analysis in this study, all methods revealed excellent detection limits that comply (with a sufficient reserve) usual environmental concentrations. The methods were relatively easy from the point of view of the plant sample preparation in terms of the available quantity of the sample and the composition of the matrix. However, the methods significantly differed in time demands and requirements for practical experiences in a running of instrumental techniques. Therefore, from a practical, routine perspective, the ICP-MS should be prioritized for this analytical task. However, the "ETV" techniques may have an irreplaceable, justified role in routine practice in special applications. The complexity and pitfalls of this instrumental connection are a challenge for analytical labs that requires a highly experienced staff and a lot of patience, especially in a protractive optimization. Great efforts are counterbalanced by the possibility to process hardly analysable, miniature or very resistant samples. SS-HR-CS-GFAAS greatly competes with the SlS-ETV-ICP-MS, especially in this field. Both the techniques have to solve the homogeneity of samples, matrix effects and a proper calibration strategy, the SlS-ETV-ICP-MS moreover difficulties in the preparation of a stable slurry. On the other hand, the preparation of slurry is a little simpler way to dilute samples with high concentrations of analyte than in the direct analysis of solid material. Some elements are not in the principle analysable using any GFAAS arrangements. A multi-analyte character of the "MS" methods shortens time demands in comparison to typically single-element "AAS" techniques. The capability of the ETV unit to solve matrix interferences at the stage of the heat treatment favours it over classical wet "MS" techniques. These reasons speak in favour of the (SlS)-ETV-ICP-MS.

The procedural limits of detection of all methods proved sufficient for Tl analysis in spruce needles and were (in μg kg^{-1}): 0.18, 0.0099, 0.024 and 1.2 for ICP-MS, ETV-ICP-MS, SlS-ETV-ICP-MS and SS-HR-CS-GFAAS.

4.2 The analyte transport efficiency in ETV-ICP-MS

Based on experiences gained in Objective 1, the analyte transport efficiency was studied and carbon microparticles (CMs) were proposed as a physical carrier to enhance the analyte transport efficiency for ETV-ICP-MS. A straightforward approach based on the analysis of slurry prepared from CMs and a sample or a standard solution was employed. The potential of CMs as a physical carrier for ETV-ICP-MS was investigated. Au and Tl were chosen as analytes. Au was considered to be an ideal element for that kind of research for its high melting point and insignificant analyte losses during pyrolysis. From the perspective of the ETV analysis, volatile Tl seems to be a more challenging task. That makes the results obtained from the study of the Tl analysis using CMs as an analyte physical carrier even more valuable. Both these elements are easily analysable by ICP-MS because no spectral interferences occur. So, all attention was focused only on the ETV processes problematics.

4.2.1 Carbon microparticles

The amount of CMs used in preliminary experiments was derived from our previous work [20], in which 0.5 mg of CA and 4 μg of Pd were dosed as a mixed modifier. 0.5 mg of CA corresponds to 0.19 mg of carbon. Equivalently, CMs (9.5 g L^{-1}) were added to the Au standard solution (0.5 μg L^{-1}) during its preparation. The analysis was carried out under the temperature programme estimated from the boiling point of Au (2856 °C) (pyrolysis 400 °C and vaporization 2700 °C). The use of CMs as a physical carrier of analyte resulted in a significant signal enhancement of 4100 %.

Based on the FE-SEM measurements of the original CMs and the CMs leaving the ETV after the temperature programme, three different carbon particle types were identified. The pictures taken by FE-SEM are given in Figure 3. The primary CMs are clusters of an approximate size from 20 to 40 μm composed of primary carbon nanoparticles (CNs) of an approximate size from 50 to 300 nm. During the thermal treatment, the secondary CMs are formed. The primary clusters fall apart into smaller clusters of an approximate size from 3 to 13 μm. Then, these secondary CMs act as analyte carriers. Carbon particles also seem to have a crystal structure.

4.2.2 Optimization and validation of ETV-ICP-MS analysis using CMs

The optimal CMs concentration of 1 g L^{-1} for the Au analysis was found. The optimized pyrolysis and vaporization temperatures were 500 °C and 2700 °C. The optimal vaporization temperature was the highest temperature investigated because of the necessity of a higher temperature for the cleaning step and to prevent the transport tube from melting at the connection to the ETV. Even if the maximum temperature that can be used in the ETV unit is 3000 °C, 2750 °C was used in this study. In the case of Tl, the optimal concentration of CMs was 2.5 g L^{-1}. The optimized pyrolysis and vaporization temperatures for Tl were 400 °C and 1900 °C. The pyrolysis temperatures were chosen slightly above the optimal ones to make a compromise between the signal intensity and the degree of sample thermal pretreatment. The optimization of pyrolysis and vaporization temperatures of Au and Tl is shown in Figure 4. The optimization of CMs concentration for Au and Tl is given in Figure 5.

Under the optimized conditions, the methods performance was evaluated by the repetitive analysis of standard solutions of Au and Tl. The result obtained for Au in the digested CRM GBW 07601 (the informatory value 2.1 ±2 μg kg^{-1}) was 2.2 ±0.1 μg kg^{-1}. The result for Tl in the digested CRM BCR 679 (the certified value 3 ±0.3 μg kg^{-1}) was 3.2 ± 0.2 μg kg^{-1} and in the slurry 2.7 ±0.1 μg kg^{-1}. The result for Tl in the CRM GBW 10052 (the certified value 57 ±11 μg kg^{-1}) was 51 ±3 μg kg^{-1}. The instrumental limits of detection were 0.016 ng L^{-1} for Au and 0.026 ng L^{-1} for Tl. The recoveries and repeatabilities measured on calibration standards were in the range 99 – 100 % and 0.2 – 2.3 % for Au and 100 – 111 % and 2.9 – 6.7 % for Tl.

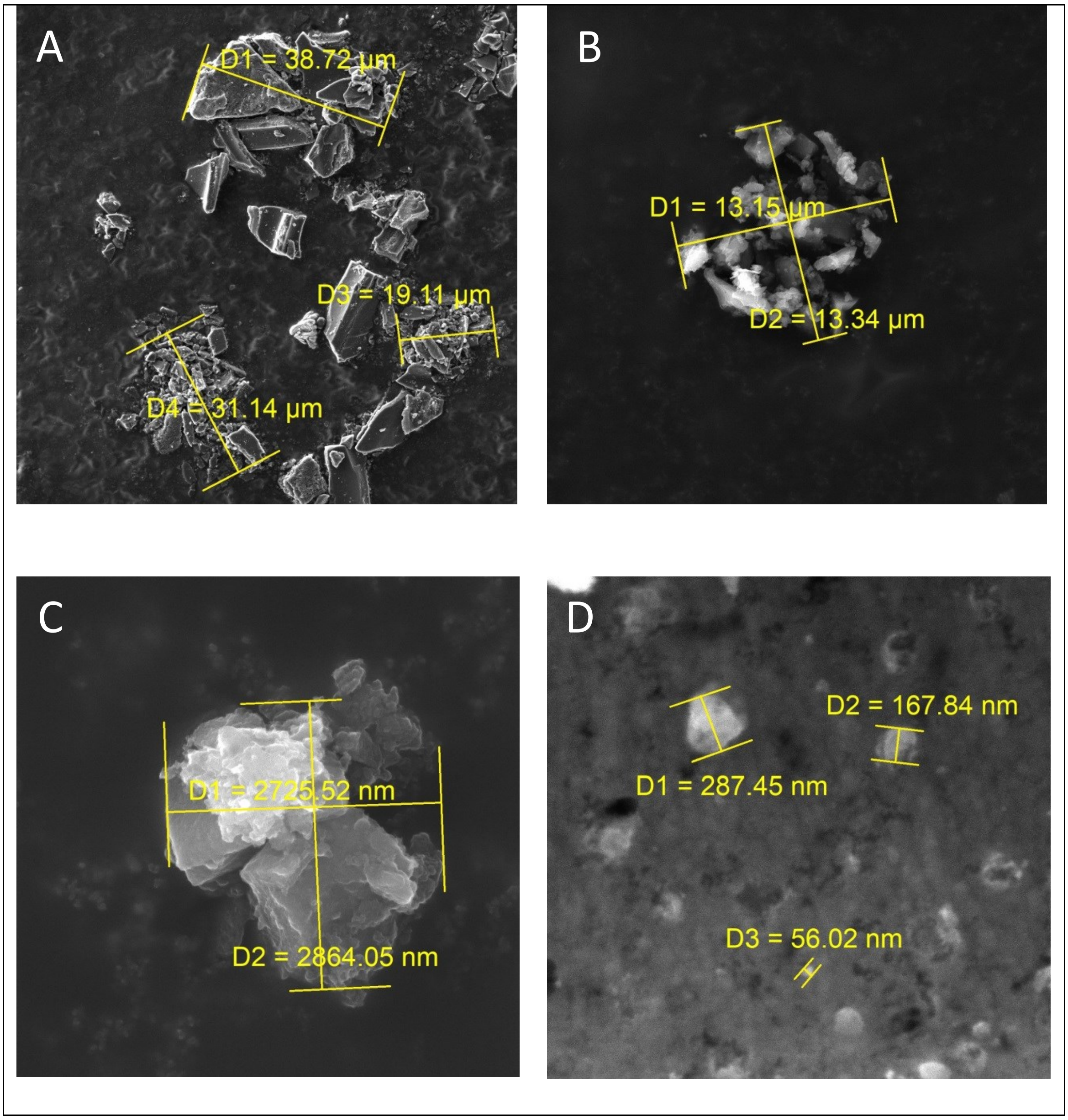

Figure 3: Pictures of carbon particles taken by FE-SEM; A - The primary clusters of CMs; B, C - The secondary clusters of CMs; D - The primary CNs

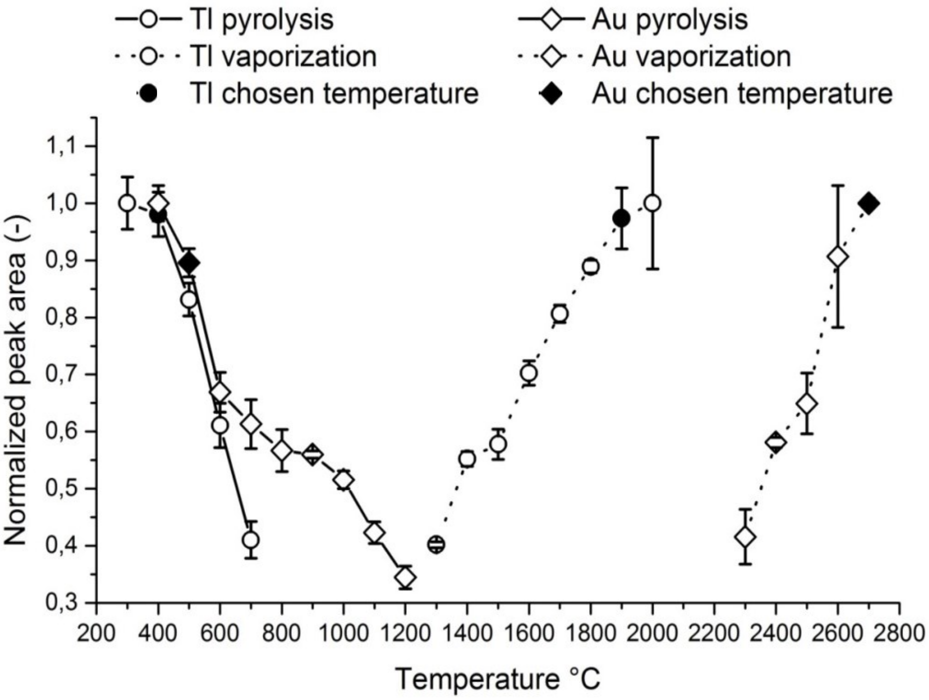

Figure 4: The optimization of temperature programme for Tl and Au

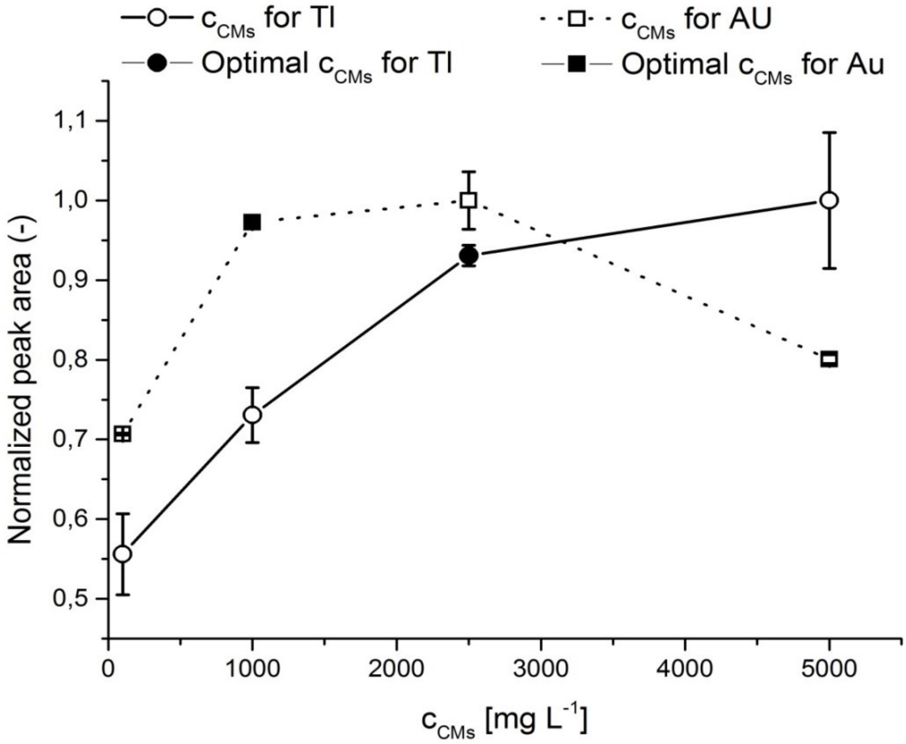

Figure 5: The CMs concentration optimization

4.2.3 Summary for the objective 2

The analytical characteristics obtained in this part of the study confirmed the usability and robustness of CMs as a physical carrier of analyte. In the case of Tl analysis, digested and slurried samples were successfully analysed under the same working conditions. This fact even further underlines the significance and influence of the transport efficiency modification. The CMs physical carrier obviously helps to overcome the possible slurried sample matrix interferences that were not properly treated during the simplified pyrolysis step. The pyrolysis temperature was kept relatively low (500 °C for Au and 400 °C for Tl) also because of a risk of analyte losses, especially Tl. The instrumental limits of detection were 0.016 ng L^{-1} for Au and 0.026 ng L^{-1} for Tl. The recoveries and repeatabilities measured on calibration standards were in the range 99 – 100 % and 0.2 – 2.3 % for Au and 100 – 111 % and 2.9   6.7 % for Tl. The use of CMs decreased the total load of carbon particles into the ICP-MS and diminished the deterioration of the sampling and second skimmer cone in the comparison to the mixed modifier CA + Pd because a lower amount of carbon is introduced into the ICP-MS.

4.3 Practical experiences with the ETV-ICP-MS prototype

During the three years' time period of the work with the instrumentation ETV-ICP-o-TOF-MS from the GBC Company, experiences regarding the analytical performance, usability and laboratory operation of this technique were gained. The ETV GF 5000 used in this work was a prototype borrowed to the Institute of Environmental and Chemical Engineering for testing in the connection to the ICP-o-TOF-MS Optimass 9500. This chapter was therefore devoted to the user evaluation of this technique regarding (i) the software used for controlling the instrumentation, (ii) the construction aspects of the ETV unit, (iii) the utilization of the full analytical potential, (iv) the economics of the routine use and (v) the user comfort with operating this technique.

4.3.1 Evaluation of software

Monitoring of the time resolved signal throughout the temperature programme

During the optimization of the ETV unit temperature programme and an amount of a modifier used, the intensity of selected isotopes is usually monitored in time throughout the entire temperature programme including pyrolysis step. This approach has been used in many cases reported in the literature [21-23]. In this way, it is possible to obtain not only the optimum pyrolysis and vaporization temperatures but also an overview of analyte losses during the temperature programme before the start of the vaporization step and the signal acquisition. The ability to monitor these analyte losses could help speed up and refine the whole optimization process. In our case, the time dependent measurement of the intensity throughout the entire temperature programme was not possible for two reasons. Firstly, only the total signal acquisition time for selected analytes could be set within the analytical sequence during which ETV and ICP-MS interact. Thus, the result was only the total signal intensity, the mean peak area related to one second of acquisition and the total peak area. No data describing the profile of the signal in time was available. Secondly, the beginning of the signal acquisition was firmly connected to the start of the vaporization step.

The dosing order of sample and modifier

The order of modifier and sample dosing can have a significant impact on the modifier proper function. A modifier can be dosed into the graphite furnace first and then dried to modify the inner surface of the graphite furnace before dosing a sample as e.g. Husáková et al reported [24]. The current software version for ETV-ICP-MS does not allow gradual and multi-step modifier and sample dosing. The dosing procedure begins by aspirating of modifier, the dosing capillary is rinsed, sample is sucked and the aspirated material is dispensed into the graphite furnace in one step, e.g. the sample and modifier at once. The software allows repeated dosing during the thermal decomposition steps. It is also possible to dose only a sample during the initial dosing sequence with the later dosing of a separate modifier. However, this is impossible in the opposite order. Each start of a new sample analysis is firmly associated with the dosing of a sample into the graphite furnace. In our previous work [20] focused on the analysis of Tl using ETV-ICP-MS, it was found that the modifier (the mixture of Pd and citric acid) worked in the best way if it was dosed into the graphite furnace and dried before a sample was dosed. With the current ETV-ICP-MS software version, such a dosing procedure is not available.

4.3.2 Evaluation of the ETV unit design

In the ETV unit GF 5000, a switching valve disconnecting the carrier gas flow passing through the graphite furnace towards the ICP-MS is not built-in. This function is usual in the pretreatment steps of the temperature programme and the cleaning step. This significantly reduces the load of pyrolysis products coming from the ETV to the ICP-MS and diminishes the transport tube clogging. The switching valve is for example incorporated in the ETV unit HGA-600MS from the Perkin Elmer Company [2].

Deterioration of cones caused by pyrolytic products

The load of pyrolytic products coming into the ICP-MS did not affect the analytical performance of this technique. No undesired deposition of carbon particles in the plasma torch injector tube was noticed. The major problems were caused in the interface connecting the atmospheric and vacuum part of the spectrometer composed of three cones (Sampler, Skimmer 1 and Skimmer 2). The Skimmer 1 was not affected but the life span of the Sampler cone was shortened. Thermal stress due to the closeness of the ICP in combination with the bombardment by carbon particles resulted in tiny holes around the cone orifice after about one year of its usage. The signal intensity decreased due to the disruption of the ion beam by the turbulent flow between the first and second cone. During the four-year work, three cones were worn in this way. The pyrolytic products significantly shortened the life span of the Skimmer 2 due to the widening of its orifice caused by gradual abrasion by carbon particles, which gradually decreased the sensitivity and resolution. The signal intensity 60000 counts s^{-1} and the resolution 2000 for the ^{238}U (1 µg L^{-1}) dropped after the first month of using the ETV unit to 40000 counts s^{-1} and resolution to 1700 and remained relatively stable for about the next three months. During the next month, the intensity dropped below 20000 counts s^{-1} and the resolution below 1300. The pyrolytic products also gradually formed a thin layer of carbon particles onto the surface of the insulating element of the Skimmer 2 cone. As a result, a high voltage discharge occurred and damaged this insulating element. It led to an immediate loss of voltage on the third cone, which prevented the proper focusing of the ion beam. During the four years of the use of this ETV unit in the connection to the ICP-MS, this problem has occurred two times, which strongly points to the ETV to be the cause of this defect. There is a lot of experience with the GBC Optimass spectrometers at the workplace where this work was created. Before the Optimass 9500, the previous model Optimass 8000 was operated for a long time and a similar problem with a high voltage discharge in the ion optics was never noticed.

Absence of a switching valve, analytical performance and operating cost of the ETV-ICP-MS

The absence of a switching valve in the ETV does not affect the quality of analysis and the reliability of the results. However, from the point of view of the economy of using this technique, it leads to several problems increasing operating costs. It is necessary to change the consumable components of the ETV-ICP-MS more frequently to ensure optimal analytical conditions. The absence of the switching valve causing the load of pyrolytic products into the ICP-MS can be seen beneficial from the point of view of the analyte transport efficiency.

The possibility of monitoring the dosing process

Another drawback associated with the ETV unit GF 5000 is the absence of the ability to control the position of the dosing capillary in the graphite furnace and the dosing process itself using the built-in camera. It has a direct impact on the quality of the analysis. Checking the position of the dosing capillary is a standard procedure in the case of ETA-AAS systems before starting a new sample sequence analysis. In our case, the ETV unit had to be partially dismantled to monitor the dosing process during its optimization at least using a dental mirror. This process could hardly be performed on a daily basis. It was usually performed once a week. However, it has proven to be inadequate. Sometimes, after several successful dosings of the sample, another sample was dosed partially on the outer surface of the graphite furnace. This problem occurred when a drop of the sample was left hanging at the tip of the dosing capillary after the sample was dosed. During the ejection of the dosing capillary out of the graphite furnace, the hanging drop was captured by the edge of the dosing orifice or on the outer surface of the graphite furnace. Furthermore, the outer surface of the dosing capillary can change during longer sample sequences, a drop of a sample would climb up the outer surface of the capillary to be subsequently trapped on the outer surface of the graphite furnace. This problem could be solved by careful cleaning the dosing capillary surface with a filter paper soaked in ethanol during analysis. Due to the absence of the built-in camera, the dosing was observed at least from above by a naked eye to check the quality of the procedure. The ETV-ICP-MS instrumentation was continuously supervised by the operator to indicate the wrong sample dosage and to exclude hardly understandable differences in results for the same sample measured in two replicates.

4.3.3 Summary of the objective 3

The positive and negative aspects of the instrumental connection of the ETV unit GF 5000 to the Optimass 9500 mass spectrometer from the GBC Company were evaluated in this study. Besides the focus on the analytical performance of the given technique, a lot of experiences with its practical operation have been gained. The ETV unit used was a prototype. The beta version of the ETV-ICP-MS control software was created by modifying the software designed to control the mass spectrometer itself. Shortcomings were found on the side of the control software, which had a negative impact on exploiting the full potential of this technique under user-friendly operating conditions and on its use for routine analysis purposes. The increase of the operating cost caused by the absence of the switching valve resulting in clogging of the ICP-MS with pyrolysis products also speaks against the routine use of this technique with the ETV unit of the current design.

5 Conclusion

In its theoretical part, the presented dissertation deals with the available instrumentation of ETV-ICP-MS and its suitable use. Attention is paid to the choice of chemical modifiers and optimization of the ETV unit temperature programme. Also, the importance of the analyte transport efficiency from ETV to ICP-MS is discussed.

The analytical performance and practical aspects of laboratory operating of the ETV-ICP-MS were evaluated. Tl was chosen because it is easily analysable by ICP-MS for no spectral interferences and hardly by ETV, so all attention was focused on the ETV processes. A real sample of spruce needles and certified reference materials of low contents of Tl were analysed. The ETV-ICP-MS analysis of solutions and slurries was compared to the classical ICP-MS solution analysis and SS-HR-CS-GFAAS technique for solid samples in terms of their analytical performance and time requirements for the entire analytical process including sample preparation and the development and validation of individual methods. Their suitability for routine laboratory use was assessed. The ICP-MS solution analysis proved to be the most appropriate for routine analysis despite the need for sample decomposition. The ETV-ICP-MS method would be advantageous for samples with a hardly decomposable matrix or containing a low concentration of analyte. It is also advantageous when analysing large sample series, which are uncomplicated, but the time required to optimize the working conditions and for the actual analysis is lower than a time required for their digestion. The procedural limits of detection of all methods proved sufficient for Tl analysis in spruce needles and were (in μg kg^{-1}): 0.18, 0.0099, 0.024 and 1.2 for ICP-MS, ETV-ICP-MS, SlS-ETV-ICP-MS and SS-HR-CS-GFAAS.

The attention was paid to the analyte transport efficiency in ETV-ICP-MS. Based on the observed behaviour of the mixed modifier Pd and citric acid, carbon particles were studied as a new analyte transport efficiency modifier. CMs physical carrier enabled the successful analysis of Au and Tl in certified reference materials. The pyrolysis temperature was relatively low in both cases and no other matrix modifier was used. Tl was successfully analysed in digested and slurry samples of the CRM BCR 679 under the same operating conditions using aqueous calibration, which further confirmed the modifier robustness. Compared to analysis without modifier, the CMs enhanced the signal of 4100 %. The instrumental limits of detection were 0.016 ng L^{-1} for Au and 0.026 ng L^{-1} for Tl. The recoveries and repeatabilities were in the range 99 –100 % and 0.2 – 2.3 % for Au and 100 – 111 % and 2.9 – 6.7 % for Tl.

The user evaluation of the ETV unit GF 5000 was carried out in terms of the design of the ETV unit and the controlling software. The software shortcomings found prevented the full utilization of the potential of this technique, in particular, the lack of variability of the dosing order of sample and modifier into the graphite furnace. The signal intensity of selected isotopes could not have been recorded in time during the whole temperature programme. As for the ETV unit design, the absence of a built-in camera for the monitoring of sample dosing and the absence of the switching valve were identified as the main disadvantages. The continuous entry of pyrolysis products from ETV to ICP-MS resulted in a significant increase in operating costs. Therefore, the use of this particular instrumentation in a commercial laboratory is questionable.

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7 The list of published works

7.1 Articles

Patočka, J.; Bendakovská, L.; Krejčová, A.; Černohorský, T.; Resano, M.; Bělina, P., Thallium in spruce needles: a comparison of the analytical capabilities of spectrochemical methods. *Analytical Methods* **2017,** *9* (4), 705-715.

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7.2 Oral presentations

Jan Patočka, Anna Krejčová, Lenka Bendakovská, Tomáš Černohorský, Analýza thallia ve smrkovém jehličí s využitím ETV-o-TOF-ICP-MS, Průmyslová toxikologie a ekotoxikologie 2016, 43 ročník, Kouty nad Desnou, 9. - 12. 5. 2016, str. 40, ISBN: 978-80-7395-981-4.

Jan Patočka, Tomáš Černohorský, Anna Krejčová, Lenka Bendakovská, Practical use of carbon nanoparticles as a transport efficiency modifier for ETV-ICP-TOF-MS, 16th Czech - Slovak Spectroscopic Conference, Luhačovice, 27. – 31. 5. 2018, sborník str. 68, ISBN 978-80-88195-06-1.

Tomáš Černohorský, Jan Patočka, Anna Krejčová, Lenka Bendakovská, New approach to matrix modification in ETV ICP-MS, 16th Czech - Slovak Spectroscopic Conference, Luhačovice, 27. – 31. 5. 2018, sborník str. 67, ISBN 978-80-88195-06-1

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7.3 Posters

Jan Patočka, Anna Krejčová, Lenka Bendakovská, Tomáš Černohorský, Development of the ETV-o-TOF-ICP-MS technique and its comparison with the o-TOF-ICP-MS technique in analysis of thallium in spruce needles, European Symposium on Atomic Spectrometry (ESAS) 2016, Eger, Maďarsko, 31. 3.-2. 4. 2016, sborník str. 208, ISBN: 978-963-9970-65-6.

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