Applications of laser ablation and electrothermal vaporization as sample introduction techniques for ICP-MS

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Abstract. The field of applications of ICP-MS can be further increased by the use of special sample introduction techniques such as laser ablation (LA) and electrothermal vaporization (ETV). In both cases a tandem source for mass spectrometry is formed by the sample introduction device and the ICP. The first source is specifically designed for the volatilization of a sample and it can be used to introduce selectively only certain parts of a sample into the ICP-MS, based either on local distribution (LA) or volatility (ETV). Applications of LA-ICP-MS are the determination of distribution patterns of minor constituents in solid samples such as ceramics, alloys or hard biological structures. Homogeneity testing in the first two types of samples or determination of distribution patterns of trace elements in the latter can be carried out rapidly with high spatial resolution on a multielement basis. The possibility of on-line separation between fractions of different volatility in a sample with ETV-ICP-MS is demonstrated for volcanic eruption products and other samples.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is applied routinely in many different fields such as material science, environmental protection, quality control and many more because of the wide range of elements covered, the low detection limits, the high sample throughput and the reliability of modern instruments in day to day operation. Much of the research and development work is directed towards better sensitivity and resolution, but sample introduction must also receive attention. The majority of analyses by ICP-MS are carried out on solutions using a conventional pneumatic nebulizer. However the type of analytical tasks which can be solved by ICP-MS can be extended using a number of other sample introduc-

tion techniques which can be easily adapted to ICP-MS, such as flow injection (FI), liquid chromatography (LC), laser ablation (LA) and electrothermal vaporization (ETV). These introduction techniques either help to overcome some of the limitations posed by the pneumatic nebulizers (i.e. total amount of dissolved solid has to be less than 0.1% m/v) or they make use of some physical properties of the sample which in turn enhances the analytical information gained during the analysis.

The reactions produced upon the interaction of laser light with a solid sample have been used for a long time for analytical purposes [1, 2]. Among the methods developed are laser microprobe optical emission spectrometry and laser microprobe mass spectrometry. The ability to focus a laser to very small spot sizes and therefore to achieve analytical results with high spatial resolution was one of the driving forces for the development of the methods, together with the fact that they can be applied to both conducting and non-conducting materials. The same is true for the use of laser ablation as a sample introduction technique for ICP-MS, where it provides one of the few possibilities to analyze solid samples directly by ICP-MS. Unfortunately the method suffers from some serious drawbacks when it comes to quantitative analysis. The ablation process is highly dependent on the nature of the sample and direct calibration is only possible when standard materials are available with a matrix similar to the sample. In such an ideal case, an accuracy of 5 to 10% is possible but in many other cases the method has to be considered as semiquantitative. The real strength of LA lies in the measurement of distribution patterns of trace elements in solid samples with high spatial resolution [3, 4]. In these cases, often only relative numbers are needed and, by using one or more of the matrix elements as internal standards, a precision of better than 10% is possible.

Filaments, platforms or tubes of high temperature resistant materials, such as tungsten or graphite, can be used as ETV devices. Several μ l of solution are deposited on the surface and the temperature is controlled by an electrical current flowing through the device. The most common devices are graphite furnaces similar to those used in GF-AAS. The most important advantages of ETV

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compared to conventional solution nebulization are the low sample consumption ($< 100 \mu\text{l}$), the higher transport efficiency and a lower level of MO^+ ions formed when aqueous solutions are analyzed. A severe drawback of the method is the relatively short transient signal of 1–2 s produced by the ETV. Only a relative small number of elements can be analyzed per cycle because the quadrupole mass spectrometer is a sequential rather than a simultaneous detector. Typical applications are the analysis of high purity reagents and the determination of Fe with a much lower detection limit because of the reduction of the interference from $^{40}\text{Ar}^{16}\text{O}^+$ with ^{56}Fe [5].

This paper shows how sample introduction techniques such as LA and ETV can be used in routine analysis in a laboratory which is dedicated both to contract work for industrial customers and research activities in cooperation with other academic research groups. Among the examples selected are the determination of distribution patterns of trace metals in hard biological structures and homogeneity testing on low alloy steel samples by LA-ICP-MS. ETV-ICP-MS has been used for the analysis of Hg in AgNO_3 at the low ng/g level and the determination of volatile compounds in products from volcanic eruptions.

Experimental

The work described was carried out using an Elan 5000 instrument in combination with a Model 320 Laser Sampler for the laser ablation experiments and a HGA-600MS for the ETV experiments (Perkin-Elmer Sciex, Thornhill, Ontario, Canada). The ICP-MS was optimized daily by adjusting the power (1000 W to 1200 W) and the nebulizer gas flow (0.8 l/min to 1.0 l/min). Plasma and auxiliary flows were kept constant at 15 l/min and 0.8 l/min, respectively. The laser ablation unit included a Nd:YAG laser, a sample stage with three computer controlled stepper motors and a video camera system for the observation of the sample. The unit was modified in various ways in order to have a more flexible and user friendly system [6]. Among the hardware modifications are a new sampling cell which allows the illumination of the sample from the top, the side and the bottom and an additional laser diode which helps to locate points of interest on the sample. Flat samples can be clamped against a ring which is perpendicular to the laser beam so that focusing is maintained throughout the analysis. In order to achieve the degree of automation needed for the determination of distribution patterns (which usually includes the analysis of hundreds of points per sample) a computer program was written controlling the laser, the sample stage and the ICP-MS. A focusing lens with a focal length of 40 mm was used throughout the work. The ETV device is based on a conventional graphite furnace for atomic absorption spectrometry (GF-AAS) with slightly different gas flows. The carrier gas stream is directed through the graphite tube during the vaporization step and the sample introduction hole is sealed with a graphite tip so that efficient transport of the analyte from the graphite furnace into the ICP is guaranteed. Pyrocoated tubes were used throughout the work (Perkin-Elmer, Norwalk, CT, USA).

LA-ICP-MS analysis was carried out using the low alloy steel standard reference materials NBS 1161–NBS 1168 (National Bureau of Standards, Gaithersburg, MD 20899, USA). For the quantitative work the laser was focused to a spot size of approximately 2 mm. The laser was fired at 10 Hz and data acquisition was started after a preablation of 30 s. For the homogeneity testing, the laser was focused to 50 μm and 10 shots at 2 Hz per point were applied. Sections of teeth and fin ray samples were prepared with a thickness of approximately 0.5 mm. This allows light transmission through the samples and therefore makes the annual lines visible on the screen. Prior to analysis, samples were washed in 10% nitric acid for a few seconds and rinsed in distilled water.

The nitric acid used in this work was re-distilled in quartz from *pro analysi* grade nitric acid (E. Merck, Darmstadt, Germany); de-ionized water from a Milli Q Plus system (Millipore Corp., Bedford, MA, USA) was used with an indicated outlet conductivity of $18 \text{ M}\Omega^{-1}$. Mercury standard solutions were prepared from a 1000 $\mu\text{g/l}$ stock solution (E. Merck, Darmstadt, Germany). All vessels were cleaned overnight prior to their use with 10% m/m nitric acid.

Results and discussion

Why are sample introduction techniques such as LA, ETV or LC in combination with ICP-MS so successful? The key word for all these systems is tandem source mass spectrometry [7]. Instead of one source being responsible for the vaporization, atomization and ionization of the sample, these tasks can be divided among two different sources as shown in Fig. 1. In the case of LA and ETV-ICP-MS, the first source is mainly responsible for the vaporization of the sample and the ICP for the atomization and ionization steps. Finally, the mass spectrometer is used for identification and quantification of the analytes. The addition of a separate source for the volatilization step provides the analytical chemist with more control over this process; this in turn means that more analytical information can be gained from the analysis. In the case of LA local analysis can be carried out by selectively ablating material from small areas on a solid sample. This spatial information is lost when the solid sample is digested prior to the analysis. An ETV

Fig. 1. The concept of Tandem Source Mass Spectrometry

device can be used to separate volatile components from refractory components of a sample using an appropriate temperature program. Typical examples of how tandem sources, such as LA-ICP and ETV-ICP, can be used to solve analytical problems are given below.

Laser ablation ICP-MS

The most severe problem with LA is the high dependence of the ablation rate upon the type of material. This makes quantitative analysis difficult in the absence of matrix-matched standards, a case frequently encountered in routine analysis. However quantitative analysis by LA-ICP-MS is possible if appropriate standards are available. A typical example is the analysis of low alloy steel where the matrix of the sample is well known. In Table 1, some results for the analysis of standard reference materials are shown using ^{57}Fe as an internal standard. Similar results can be achieved by spark emission measurements. Standard addition calibration and external calibration can be applied to the analysis of powdered samples which can be pressed into pellets but the technique is time consuming because of the homogenization step involved [8]. In the absence of standards, semiquantitative results can be produced with a relative precision of between 30 and 80%; this is in many cases still sufficient especially if the inhomogeneity of environmental samples such as soils is considered [9].

The unique strength of LA lies in the determination of distribution patterns of minor and trace elements in solid samples with high spatial resolution. For this type of analysis relative rather than quantitative numbers are needed and therefore no standards are required. The method offers a spatial resolution of 5 to 50 μm (depending on the wavelength of the laser) and multielement analysis with detection limits at the sub $\mu\text{g/g}$ level for conducting and non-conducting materials can be performed. However, in order to measure distribution patterns on a routine basis, a high degree of automation is required since hundreds of points must often be analyzed to fully characterize a sample. A software program has been developed which permits the automated analysis of up to 500 points; all of the laser parameters (laser energy, pulse mode, spot size, frequency and number of the laser shots per spot) can be specified for each single point [6]. Two typical applications are the determination of trace

metals in hard biological structures and homogeneity testing of alloys and ceramics.

There are many biological structures which accumulate or grow incrementally over the life span of an organism. If materials deposited in those structures are not subject to migration or chemical breakdown, the tissue will retain a historical record of exposure to a variety of substances. Structures which have the potential to be used in this fashion include fin rays from fish, shells of marine and freshwater bivalves, tree cores and teeth from a variety of mammals. An additional benefit of these hard structures over soft tissues is that they are not affected by bacterial breakdown over long periods of time. Samples which have been preserved for decades or centuries can increase greatly the historical record available. However this wealth of historical information on environmental change can be easily obtained only via solid sampling techniques such as LA-ICP-MS. The analysis of a fin ray from a sturgeon which was more than one hundred years old when it was captured in Canada can serve as an example of the potential of the method. The animal lived in an area where a lot of mining commenced during the life span of the fish and the goal of the experiment was to find the traces of these anthropogenic activities in the fin ray. More than 100 points were analyzed on the cross section of the fin ray with a spatial resolution of approximately 50 μm . 20 shots in the Q-Switch mode were fired at a frequency of 1.5 Hz on each spot. While firing the laser at higher frequencies produces a more stable signal, lower frequencies should be used with hard biological structures, which tend to form cracks when the laser is firing at 10 Hz; this is most probably because they cannot dissipate the heat deposited in the sample fast enough. A typical signal for one spot is shown in Fig. 2. A total number of 8 elements was measured from which only 3 are shown: ^{44}Ca which was used as an internal standard, ^{107}Ag and ^{202}Hg . Since the laser was moved perpendicularly to the annual lines, temporal changes in the contents of trace metals can be measured as is shown in Fig. 3 for Ag. The concentration of Ag in the fin ray increased between 1900 and 1950 by two orders of magnitude which coincides with the quantity of the silver mining activity in this area. Similar measurements have been carried out analyzing teeth from walrus and beluga whales from the Canadian arctic. Despite the fact that these animals live remote from any anthropogenic source of heavy metals such as Cd and Pb, contents of these elements in soft

Table 1. Results for the analysis of a low alloy steel standard reference material (NBS 1162) by LA-ICP-MS using NBS 1161, 1163, 1164, 1165, 1166, 1167 and 1168 as external standards and ^{57}Fe as an internal standard. All concentrations are given in $\mu\text{g/g}$. Operating conditions: ICP-MS: 1100 W, nebulizer gas flow 1 l/min, dwell time 50 ms, 100 replicates; Laser: Q-Switch Mode, laser energy 95 mJ, laser repetition rate 10 Hz, spot size diameter 2 mm

Element	Cert. value	LA-ICP-MS $\pm$ std. dev. (n = 3)	Regression coefficient	Calibration range
V	580	598 $\pm$ 75	0.9972	20-1700
Cr	7400	7580 $\pm$ 615	0.9980	40-7400
Co	1100	1135 $\pm$ 45	0.9992	80-2600
Cu	2000	1850 $\pm$ 159	0.9914	190-3400
Mo	800	775 $\pm$ 59	0.9935	50-3000

tissues such as kidney are very high. Levels of up to 100 $\mu\text{g/g}$ of Cd are not uncommon [10]. In order to clarify whether these elements have been accumulated over a long period of time through the food chain or whether the problem is related to anthropogenic activities, teeth from different time periods starting one or two hundred years ago up to the present should be analyzed. So far only preliminary results can be presented. Among the most interesting are distribution patterns of Pb in a walrus tooth, as shown in Fig. 4. The highest Pb concentra-

tions are always found in the oldest part of the tooth which means that the animal takes up much more Pb in its infancy. Probably this is related to the breast feeding in this period; the milk is the source of the Pb. The Pb concentration drops dramatically later in life when the nutritional behaviour changes. These two examples illustrate how valuable LA-ICP-MS can be for the determination of distribution patterns of multielement traces in hard biological structures.

Homogeneity testing is another possible application for LA-ICP-MS. In order to validate the method, a low alloy steel sample (NBS 1162) was analyzed for 6 elements using ^{57}Fe as an internal standard. The ratio of $\text{cps}(\text{analyte})/\text{cps}(^{57}\text{Fe})$ can be used to visualize the degree of the homogeneity of the distribution of the analyte element. The laser was focused to a spot size of 50 μm and 10 shots at 2 Hz were fired per site in the Q-Switch mode analyzing 100 points separated by 0.5 mm from each other on an area of 5 mm by 5 mm. All elements had to be measured with reduced sensitivity in order to prevent saturation of the detector and since this reduction was different for each element the ratios of the intensities given in Figs. 5 and 6 are not directly related to the ratios of the concentrations. Elements which are soluble in iron, such as Cr, Co or Ni, are homogeneously distributed as the surface plot for Ni in Fig. 5 shows. The relative standard

Fig. 2. Analysis of a fin ray from a sturgeon with LA-ICP-MS. Operating conditions: ICP-MS: power 1000 W, nebulizer gas flow 1.0 l/min, dwell time 20 ms; Laser: Q-Switch Mode, laser energy 70 mJ, laser repetition rate 1.5 Hz, spot size diameter approximately 50 μm , 20 pulses

Fig. 3. Changes in the intensity of signal of ^{107}Ag in a fin ray from a sturgeon between 1900 and 1950. Experimental conditions as in Fig. 2

Fig. 4. Distribution of Pb in a walrus tooth of a 30 year old animal. Operating conditions: ICP-MS: power 1000 W, nebulizer gas flow 1.0 l/min, dwell time 20 ms; Laser: Q-Switch Mode, flash lamp energy 70 mJ, Q-Switch delay 300 μs , laser repetition rate 2 Hz, spot size diameter approximately 200 μm , 23 pulses

Fig. 5. Nickel distribution in a low alloy steel (NBS 1162). Operating conditions: ICP-MS: power 1000 W, nebulizer gas flow 1 l/min, dwell time 20 ms; Laser: Q-Switch Mode, laser energy 70 mJ, laser repetition rate 2 Hz, spot size diameter approximately 50 μm , 10 shots, 100 points analyzed

deviation (RSD) of all 100 points for the ratio $\text{cps}(^{60}\text{Ni})/\text{cps}(^{57}\text{Fe})$ is 4.7%. Nb is added to steel together with Ti and/or V to bind carbon as metal-carbide. These compounds are not soluble in iron and they form discrete metal-carbide crystals. Consequently, these elements are distributed inhomogeneously as can be seen in Fig. 6 for Nb with a RSD of 98% for the ratio $\text{cps}(^{93}\text{Nb})/\text{cps}(^{57}\text{Fe})$.

Electrothermal vaporization ICP-MS

Among the advantages of an ETV as a sample introduction technique for ICP-MS are the high transport efficiency compared to conventional solution nebulization and the lower partial pressure of oxygen in the plasma, which consequently lowers the MO^+/M^+ ratio. Additional benefits occur because the ETV is part of a tandem source; applications which are very different from the GF-AAS type of analysis are possible. The sample only has to be vaporized not atomized and therefore separation of species on the basis of their volatility is possible [11]. The transport efficiency can be further increased in the presence of a matrix element. It has been shown that better sensitivity and reproducibility of ETV-ICP-MS measurements can be achieved by adding compounds such as NaCl or PdNO_3 as matrix modifiers [12]. The matrix modifiers act as carriers for the vaporized analyte elements preventing them from condensing in the transfer lines between the ETV and the ICP. However there is an optimum amount of matrix modifier which should not be exceeded because then signal depression due to the matrix effects and spectral interferences due to molecular ions formed by the matrix modifier both occur [13]. Matrix matched standards must be used to ensure that these two effects have the same magnitude for standards and samples if an external calibration is to be used for quantitative analysis. Since this can not always be guaranteed, calibration by standard addition is preferable in cases such as the determination of mercury in AgNO_3 . The Hg concentration in AgNO_3 , for photographic purposes, has to be below $0.1 \mu\text{g/g}$; this means that the detection limit of the analytical procedure should be better than $0.02 \mu\text{g/g}$. Analysis of AgNO_3 solutions either directly or by flow injection is not sensitive enough especially if one considers the severe memory effects associated with Hg and the dilution factor of 100 to 1000 involved. The cold vapour technique is also not applicable because of the formation

of an amalgam during the reduction step. ETV-ICP-MS can solve the analytical problem using the temperature program given in Table 2. Selective vaporization of the Hg was used because of the matrix effects induced by the large excess of Ag. Hg can be vaporized at 800°C , a temperature where almost no Ag is vaporized as can be seen from Fig. 7. If a vaporization temperature of 1200°C is selected, the sensitivity of the Hg signal (peak area) is decreased by 25%. Obviously it is very difficult to get matrix matched standards for such a case and therefore standard addition calibration was used. A detection limit of $0.01 \mu\text{g/g}$ of solid AgNO_3 was achieved by analyzing 1% AgNO_3 (g/100 ml) solutions.

Thermal vaporization can be found in nature on a large scale in the form of magma degassing which can be considered as the big brother of ETV. Large amounts of

Table 2. ETV Temperature program for the determination of Hg in AgNO_3

Temperature [$^\circ\text{C}$]	Ramp [s]	Hold [s]	Vaporized species
90	5	5	
110	20	1	H_2O
800	0	2	Hg
2650	1	2	Ag
20	1	10

Fig. 7. ETV-ICP-MS signal for 10 ng/ml Hg in a 1% (g/100ml) AgNO_3 solution. $10 \mu\text{l}$ solution injected, ^{107}Ag was measured with reduced sensitivity. Operating conditions: ICP-MS: power 1000 W, nebulizer gas flow 0.8 l/min , dwell time 10 ms; ETV (see Table 2)

Fig. 6. Niobium distribution in a low alloy steel (NBS 1162). Operating conditions as in Fig. 5

Fig. 8. Evaporation of trace metals from a basaltic lava (Fujiyama, Japan). Operating conditions: power 1200 W, nebulizer gas flow 1 l/min, dwell time 20 ms

gases are released from silicate melts (magmas) during the eruption of volcanoes such as Mount St. Helens in 1980 or Pinatubo in 1992. It is believed that heavy metals are emitted in the form of clusters containing only a few molecules, mostly chlorides and fluorides; these are very volatile at temperatures between 700°C and 1200°C compared to the oxides or carbonates of these elements [14, 15]. Parts of these compounds can still be found as inclusions in crystallized minerals and the glassy, ground mass of lava, bombs and ashes. In order to determine these included gases and aerosols and to simulate the conditions in a volcano, the volcanic material was ground to a mean particle diameter of approximately 500 µm and then analyzed by ETV-ICP-MS. This was carried out by placing 50 to 100 mg of lava into a graphite boat which was positioned in the middle of the graphite tube. The temperature was then raised to 1000°C over 5 min and 20 elements were analyzed during this process. The temperature in the sample is considerably lower than the nominal temperature set by the software because it is cooled by the carrier gas flowing at 1 l/min through the furnace. Temperature differences of roughly 200°C from a nominal temperature of 1000°C have been measured. Figure 8 shows the signals recorded for a basaltic sample from Fujiyama (Japan) for the elements Cu, Hg and Pb with corrected temperatures. The peak maximum for Hg is already reached at 200°C; this is not surprising although the maxima of 770°C for Cu, Pb and a number of other elements is surprisingly low. Emission is only observed during the first heating cycle. These are temperatures which are common in volcanoes and therefore it might be expected that this is an important source for the emission of heavy metals into the environment. Further investigations are planned in order to identify the molecular composition of the volatile species by coupling the ETV directly to a mass spectrometer.

Conclusions

Laser ablation and electrothermal vaporization are two sample introduction techniques for ICP-MS which help to solve unique analytical problems which could not be

solved using only conventional solution nebulization. Both form, together with the ICP, a tandem source for mass spectrometry. Additional information about the sample can be gained because of the possibility of introducing only part of the sample into the ICP depending either on its location in the solid sample (LA) or its volatility (ETV).

LA can be used for quantitative analysis if matrix matched standards are available but for this type of application the method has to be compared to other well established instrumental methods such as X-ray fluorescence (XRF) which are clearly superior when it comes to precision and automation. The advantages of LA-ICP-MS compared to XRF are better detection limits, simpler spectra and higher sensitivity for the light elements but the application of the method is often hampered by the absence of suitable standard reference materials. On the other hand, very good results can be achieved in the semiquantitative mode. The full potential of the method can be used for the determination of distribution patterns in solid samples with a high lateral resolution as has been shown for trace elements in hard biological structures or for the homogeneity testing of solid industrial materials. The method compares favorably with other techniques, such as electron microprobe, because of its low detection limits, the wide range of elements from Li to U measurable and independence from the electric conductivity of the sample. Further improvements in terms of spatial resolution and especially in producing quantitative results can be expected.

The applications of ETV-ICP-MS can be separated in two groups: (i) analysis of very small sample volumes and the determination of elements such as Fe with which oxygen containing molecular ions interfere and (ii) the determination of volatile parts of a sample using an appropriate temperature program which separates on-line these compounds from the refractory parts. (i) is very similar to the well established GF-AAS technique but (ii) makes full use of the tandem source concept and therefore gives new insights into the nature of the samples analyzed. A typical example is the determination of volatile compounds in volcanic eruption products.

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