M. I. Szynkowska,
K. Czerski,
Tadeusz Paryjczak,
*Edward Rybicki,
**Andrzej Włochowicz

Institute of General and Ecological Chemistry,
Technical University of Łódź
ul. Żeromskiego 116, 90-924 Łódź, Poland

*Institute of Textile Architecture
Technical University of Łódź
ul. Żeromskiego 116, 90-924 Łódź, Poland

**University of Bielsko-Biała,
ul. Willowa 2, 00-000 Bielsko-Biała, Poland

Testing Textiles Using the LA-ICP-MS-TOF Method

Abstract
The LA-ICP-TOF-MS method (Laser Ablation Inductively Coupled Plasma Time of Flight Mass Spectrometry) is an analytical technique for determining trace elements and their isotopes in solid samples. The action of a high-energy laser beam on a solid results in the evaporation and removal of material in the form of neutral atoms and molecules, as well as, positive and negative ions from the solid surface exposed to this radiation. In chemical analysis, the pulse laser based on a solid such as neodym (Nd:YAG) has proved to be very useful as it makes it possible to incorporate solid samples directly into plasma. It has been utilised as a source of very high energy with specific properties, and can be used to analyse various solids (conductive and non-conductive) with various sizes and shapes, where the laser beam can be focused on a very small surface with exceptionally precise location, while the evaporated material can be immediately analysed. This technique has been successfully used to analyse the elemental composition of the Wawel Castle's arras pieces, where the maximum amount of information was obtained with negligible damage to the samples. The following elements have been discovered: Ag and Au (derived from strip) and Li, Al, Cr, Cu, Zn, Rb, Sr, Sn, Ba, Ce, Hg, Pb, Bi, U (mainly in fabrics). The LA-ICP-MS-TOF method is finding growing application in the analysis of geological, environmental and forensic samples. An attempt was made to apply this technique for testing textiles, especially historical ones.

Key words: *elemental analysis, historical textiles, Wawel, Cracow.*

Introduction

Historic textiles represent a very important part of material culture. They give us not only the knowledge of social history, artistic trends and international trade, but also information about technological progress. These textiles may be composed of many different fibres, the most common of which are silk, wool, cotton, linen and other man-mades. The arrases in Wawel Castle, which are a Polish national treasure, were made from natural fibres such as silk and wool, and dyed with natural dyes. Zygmunt II August, the King of Poland and the last descendant of the Jagellonian dynasty, purchased 170 arrases in Brussels workshops for the interior decoration of castles and palaces in the second half of the 16th century. After a stormy history, 142 of them have survived to today [l].

Unfortunately, the natural raw materials used for making arras are susceptible to the action of micro-organisms, especially fungi [2]. Biological damage caused by the enzymes generated by micro-organisms shows changes in the morphological structure of fibres, decomposition of molecular and supermolecular structures, as well as changes in colour [3].

In addition, all textiles become fragile with age and inappropriate environmental conditions. Light, temperature, relative humidity, dustiness and air pollution promote the deterioration of textile materials. Hence, conserving and protecting them against devastation by all these factors is a very serious challenge for conservators.

Analytical science can play an important role in characterising fibre behaviour,

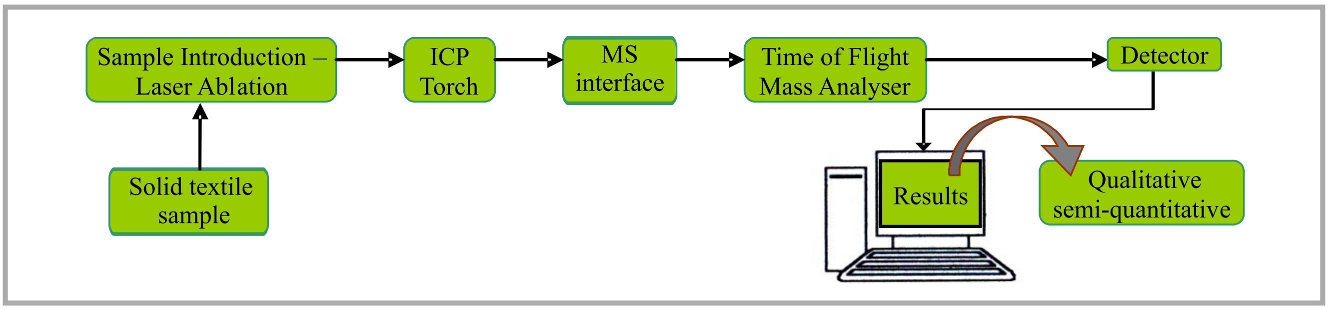

Figure 1. *A block scheme of LA-ICP-TOF-MS.*

Table 1. *Set of parameters for the LA-ICP-TOF-MS system for testing the Wawel arrases [8].*

Laser Parameters		ICP		TOF-MS			
Laser power:	> 7.5 mJ per shot (85%)	X position:	11.2 mm	Skimmer:	-1500 V	Fill:	-40 V
Pulse rate:	20 Hz	Y position:	-1.1 mm	Extraction:	-1100 V	Fill Bias:	0 V
Spot size:	150 μm	Z position:	-0.1 mm	Z1:	-770 V	Fill Grid:	-18 V
Scan rate:	100 μm/s	Nebulizer Flow,	0.79 l/min	Y Mean:	-160 V	Pushout Plate:	720 V
Distance between lines:	1000 μm	Plasma Flow:	10.0 l/min	Y Deflection:	2 V	Pushout Grid:	-580 V
		Auxiliary Flow:	1.0 l/min	Z Lens Mean:	-1030 V	Multiplier Gain:	2850 V
		Power:	800 W	Z Lens Deflection:	-2 V	Reflectron:	699 V
				Lens Body:	-130 V		

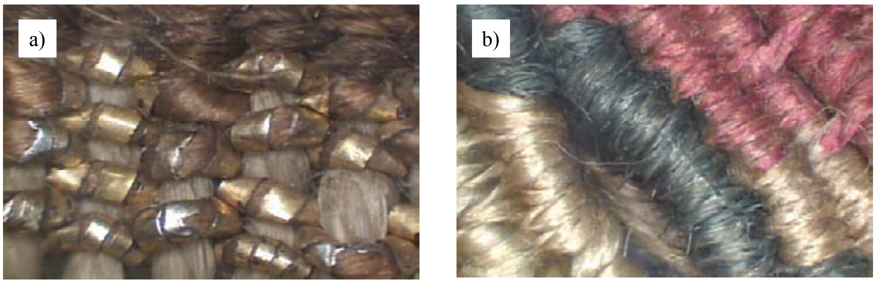

Figure 2. *Tested pieces of the Wawel arrases a) containing metal threads, b) dyed.*

Figure 4*. Laser ablation line scan.*

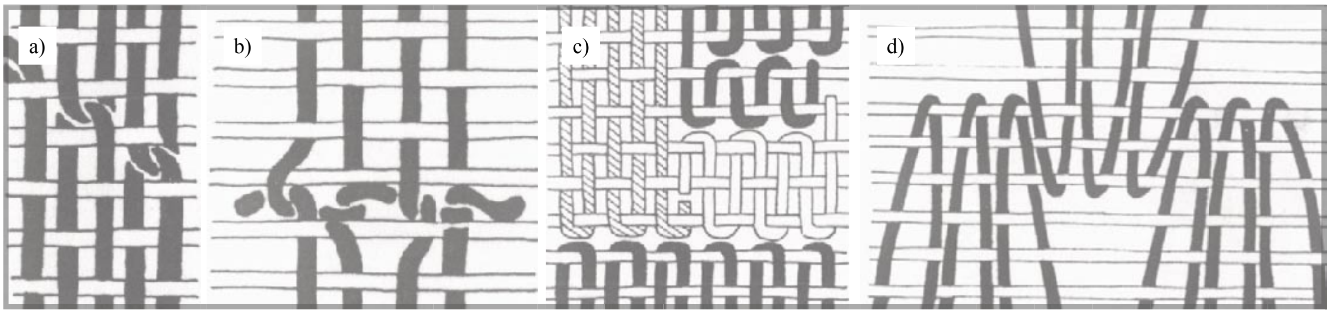

Figure 3. *Characteristic weaves of the structure of Wawel's arrases such as simple knotting (a), double knotting (b), splits (c), group equalising gathering (d) [9].*

identifying textile materials and assessing their deterioration and the conditions and risks for preserving them.

Recently, many different modern techniques for investigating the chemical and physical properties of ancient textiles have been published. For example, SEM-EDX has been used for understanding the deterioration of the textile materials and detecting of metallic mordants. These techniques are called non-destructive (ND) methods, because they are used to investigate the historical textile materials while not causing destruction to them [4].

Another such technique is the Laser Ablation Inductively Coupled Plasma Time of Flight Mass Spectroscopy (LA-ICP-TOF-MS). This is a very attractive analytical technique used to determine trace quantities of elements and their isotopes in solid samples. In the chemical analysis, a pulse laser based on a solid such as neodymium (Nd:YAG) has proved to be extremely useful as it enables the direct introduction of solid samples into plasma. It is used as a source of high energy with special properties intended for various applications, including analyses of different solids of various sizes and shapes, where the laser beam can be focused very precisely on a very small sample surface, while the evaporated material can be immediately analysed [5 - 7]. Currently, LA-ICP-MS-TOF is finding growing application in the analysis of various samples such as geological, environmental and forensic samples.

The main aim of this work was to examine and investigate the elemental composition of the Wawel arrases in order to understand the nature of these textiles. Our studies aimed to obtain the most information possible with negligible damage to the tested samples. For the first time, an attempt was made to use this unique LA-ICP-MS-TOF method in a semi-quantitative and comparative analysis of the metal content in textiles. As the object of the studies, original samples of Wawel tapestries obtained from the store of the National Museum in Cracow was chosen. The pieces were analysed without any preparation, as supplied. From historical sources, it is known that gold or silver strips were quite often spun into the tapestry structure, so we expected to confirm the presence of these metals (Au, Ag) and additionally obtain information about the presence of other elements within the mass range from 6 to 238 amu (atomic mass unit) in the samples of the arrases.

Experimental

Apparatus

In these studies we used an Optimass 8000 ICP-TOF-MS (Inductively Coupled Plasma Time of Flight Mass Spectrometer) produced by GBC (Australia) with a laser ablation unit (LA) produced by CETAC Laser Ablation System (USA). The block scheme of the apparatus is presented in Figure 1. The action of a high-energy laser beam on a solid results in the evaporation and removal of material in the form of neutral atoms and molecules, positive and negative ions from the surface of the solid exposed to this radiation. The use of a TOF analyser in the ICP-MS method allows all the elements contained in the sample under testing to be detected simultaneously.

The Wawel arrases' samples were placed inside an enclosed chamber called the ablation cell, and a laser beam was focused on the surface of arrases. When the laser is fired, a cloud of particles is produced. These particles are removed from the sampling cell by an argon carrier gas, and are swept into the ICP plasma torch for atomisation and ionisation. Next, ions of all the elements present in the sample are transferred to the TOF analyser (Time of Flight Analyser) through an MS interface which connects ICP plasma (atmospheric pressure) with the TOF analyser (vacuum pressure of about 2-3 μTorr). When these ions reach the TOF analyser, they are pushed out by an orthogonal accelerator and go through a reflectron, finally reaching a detector. The time needed to reach the detector is strictly linked to the value of mass-to-charge ratio (m/z), so the lightest ions reach the detector first, and are followed by the heavier ones. As a result the mass spectrum is obtained.

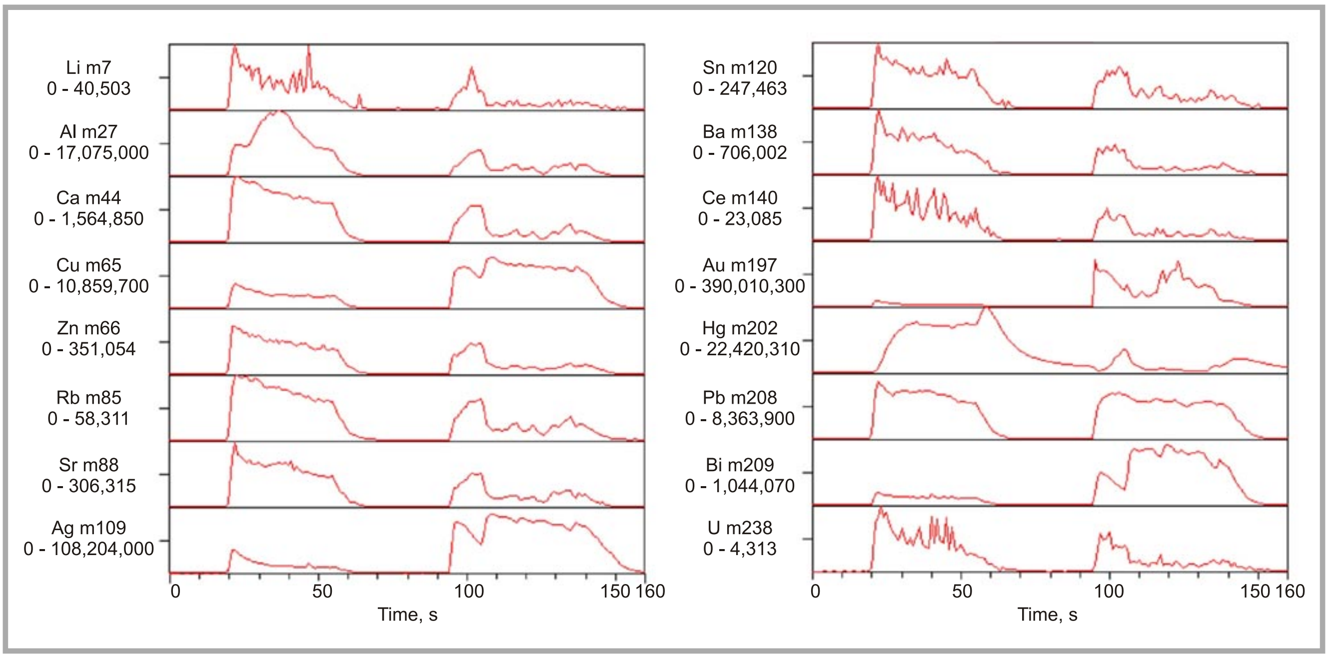

Figure 5. Time scan of a number of elements present in arrases over the line-scanned area with the intensity characteristic for each element; the particular scans are described by the chemical symbols, the isotopic atomic weights, and the relative intensity of ions or isotopes below them.

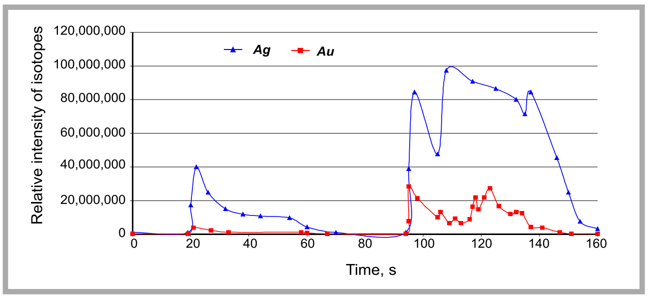

Figure 6. Line scan of Ag and Au present in metal strips.

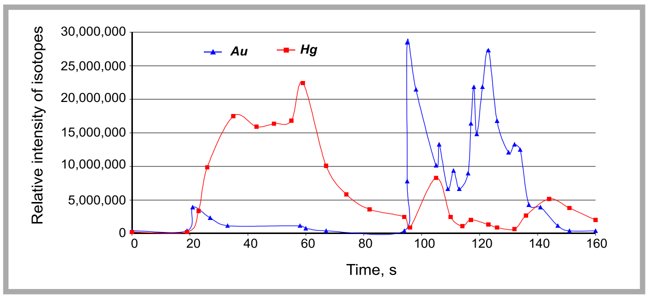

Figure 7. Relative intensity of Hg and Au ions present in fiber thread with and without gold strip.

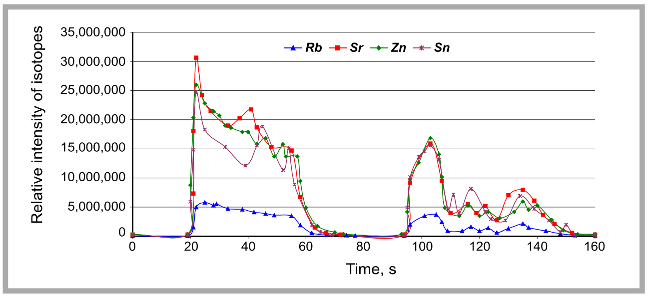

Figure 8. Line scan of Rb, Sr, Zn and Sn.

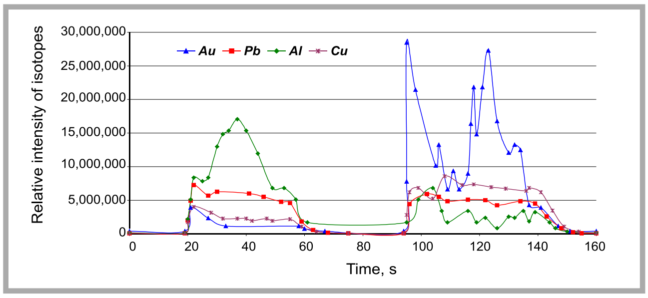

Figure 9. Line scan of Au, Pb, Al and Cu.

Table 1 presents the set of parameters used for the LA-ICP-TOF-MS for testing the Wawel arrases.

Samples tested

The tapestry samples were obtained from the store of the National Museum in Cracow and studied as supplied. The examples of the tested pieces of the Wawel arrases are presented in Figure 2. Some of the pieces studied contained metal threads (a), while others were only dyed (b).

Methodology

Each tested piece of the Wawel arrases was about 3×3 cm. The pieces were put into an ablation cell. The laser power was >7.5 mJ per shot (85% maximum laser power).

The samples were scanned along the ablation line for 160 seconds at a scan speed of 100 µm/s, so the total length of scan line was 16 mm.

Results

Sample structure

The microscopic analysis of this structure disclosed several characteristic weaves such as simple knotting, double knotting, splits and group equalising gathering, presented in Figure 3.

The diameter of threads present in the samples investigated are as follows:

- warp c. 860 µm,

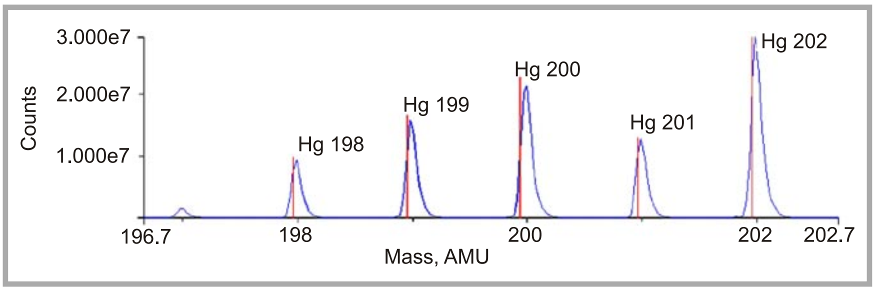

Figure 10. *Hg isotopes present in ecru weft (part of mass spectra).*

- weft c. 170-640 μm dependent on colour,
- thread with gold strip c. 620 μm,
- thread with silver strip c. 430 μm.

The LA-ICP-TOF-MS analysis

The TOF analyser provides a true multi-elemental capability for these rare and valuable samples. This maximises the information that can be gathered while minimising the sample damage. A time scan of the number of elements over the line-scanned area presented in Figure 4 (see page 88) was obtained (Figure 5 - see page 89). The total length of the laser ablation line scan was 16 mm. The following elements were discovered in the tapestry samples: Ag, Au, Li, Al, Cr, Cu, Zn, Rb, Sr, Sn, Ba, Ce, Hg, Pb, Bi and U. The presence of most elements in wool of different origins is confirmed by our previous studies [10]. The difference of relative intensity, which is characteristic for each element, of the particular element's spectrum and which changes over the time of scanning (160sec.) is connected with the fabric's structure. Based on an elemental analysis of the obtained results, we can see that the presence of: Ag and Au derives from strips, and Hg, Sn, Sr, Zn, Al and others mainly derive from the woven fabric, as shown in the diagrams presented in Figures 6, 7, 8, and 9 - see page 89).

The results of the studies demonstrate the particularly large participation of mercury in the structure of the arrases examined. Considering that in the Middle Ages gold was mostly obtained by the method of creating an amalgam with mercury, and then obtaining the pure metal by vaporising the mercury, the large relative intensity of this element in the fabric cannot be doubted. The diverse courses of the change in the intensity for Au and Hg due to the time of scanning (length) prove that Hg is mostly present in all the fabric's structure, and is not connected with gold. This phenomenon probably results from the evaporation of mercury from the surface of gold strips over a period of several hundred years and the subsequent absorption of this element by the wool and silk fibres. A similar mechanism was observed in a PhD thesis concerning the sorption and desorption of volatile pollution of the air with formaldehyde and styrene by textile furnishing products [11]. This effect may also originate from antibacterial agents containing mercury, such as were often used in the Middle Ages. Figure 10 shows an example of a part of the mass spectrum with different Hg isotopes present in the selected ecru weft. In Table 2 the relative intensities of Hg ions present in different weft types are presented.

Table 2. *Relative intensity of Hg ions present in different type of weft.*

Type of weft	Relative intensity of Hg ions
thread with Ag strip	~ 56,000
thread with Au strip	~ 210,000
ecru thread	~ 30,000,000
brown thread	~ 11,500,000
dark green thread	~ 7,000,000
light green thread	~ 1,300,000
indigo thread	~ 3,000,000

Conclusions

The results obtained in the present work reveal the great potential of the LA ICP-TOF-MS technique in yielding data concerning the elemental composition of fabrics as well as unique works of art. Combining the laser ablation and TOF analyser in the ICP-MS method allows the simultaneous detection of all the elements contained in the sample under testing with negligible damage to the samples. This method may thus be used for the quasi-non-destructive analysis of solid samples of textiles. The main advantage is that direct chemical information from the solid material can be obtained, and solids of any shape and matrix can be analysed. The samples studied do not need any preparation, which saves much time when conducting the analysis. Because it is difficult to select standards and certificate materials for suitable solid samples, this method permits mainly semi-quantitative and comparative analysis (the comparison of the intensity of peaks). The limited availability of solid textile standards is the main disadvantage of using this technique in quantitative studies.

Acknowledgments

- *The authors gratefully acknowledge the assistance of Dr A. Flynn Saint from GBC for taking part in the LA-ICP-MS-TOF studies, and of Dr M. Cybulska for her assistance in identifying the sample's structure.*
- *The financial support of this work by the Polish State Committee for Scientific Research (grant 3 T09 B 048 29) is gratefully acknowledged.*

References

1. *Holc J., Włochowicz A., The Arrases of Wawel, the Polish Royal Castle in Krakow, Fibres & Textiles in Eastern Europe, vol. 13, No. 6(54), pp. 85 - 87, January/December 2005.*
2. *Błyskal B., Ph.D. thesis, Academy of Economics, Kraków 2005.*
3. *Research report within the project No. 4 TO8E 047 22 (in Polish) carried out under the direction of A. Włochowicz, financially supported by the Polish State Committee for Scientific Research, University of Bielsko-Biała, 2005.*
4. *Abdel-Kreem O., El-Nagar K., JTATM, vol.4 (4) 2005.*
5. *Szynkowska M.I., Flynn Saint A., "Potential application possibilities of the TOF-SIMS and LA-ICP-MS-TOF methods in the research into works of art" (in Polish), Proceedings of the 'Chemical analysis in preservation of historical monuments' – Conference, Warsaw, December 2005.*
6. *Szynkowska M.I., Czerski K., Paryjczak T., Rybicki E., Włochowicz A., 'The use of the ICP-MS-TOF method with laser ablation for testing textiles', Proceedings of the ECOTEXTIL2006, 7th International Conference, Ustron, May 2006.*
7. *Szynkowska M.I., Czerski K., Paryjczak T., Rybicki E., Włochowicz A., LAB, (5), 24-26 (2006).*
8. *LA-ICP-MS-TOF Manual Instruction , GBC.*
9. *www.kobidz.pl, Leksykon włókiennictwa, M. Michałowska, Warszawa, 2006.*
10. *Leśniewska E., Szynkowska M. I., Albińska J., Paryjczak T., Rybicki E., 'An application of ICP-AES method in determining chosen elements in wool samples', Chemical Products in Agriculture and Environment, (ed. H. Górecki, H. Dobrzański), vol. 4, 616-621, 2003.*
11. *Cieślak M., Ph.D. Thesis, Technical University of Lodz, 1996.*

Received 20.07.2006 Reviewed 03.11.2006