

# LA-gf-ICP/MS (Laser Ablation- great format- Inductively Coupled Plasma / Mass Spectrometry) a new analytical tool with high spatial resolution without sampling for material characterization of manuscripts.

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## 1. Introduction

Material characterization of artworks provides information not only about the composition and structure of the pieces but also about the processes that affect or could be applied to them (and the consequences related to these processes).

Two main characteristics of the artworks must be taken into account in the design and application of analytical procedures: the inherent heterogeneity of the pieces (at macroscopic and microscopic level) and the need to maintain their physical integrity. In the study of manuscript, another aspect appears important: the spatial resolution of the methodology applied.

Manuscripts wrote on paper with iron gall ink are sensitive to acidity and iron activity (Fe +2). Degradation involves cellulose oxidation and hydrolysis. The aqueous treatment is usually applied during restoration process and partial solubility of the ink and migration of iron is essential for ulterior preservation of the document (1-2). To know initial dissemination of iron ions placed in paper structure, before whatever treatment, submits useful information. Data of dissemination of iron ions from the ink after bath complete the study.

The **objective** of this study is to evaluate the capability of a new instrument “Laser Ablation- great format- Inductively Coupled Plasma / Mass Spectrometry (LA-gf-ICP/MS)” for manuscripts characterization.

## 2. Experimental.

Manuscripts analysed: The study was applied in two different samples of manuscripts:

- M. 98 (XIX century) : pH= 5.5; 65 g/m<sup>2</sup>; 120µ; Raw Material (60% linen, 40% hemp; 20% sulphite treatment; gelatine ; Ink (iron II potassium oxalate trihydrate)
- Instrumentum (XVII century): pH=6.3; 85 g/m<sup>2</sup>; 180 µ; Raw material (75% linen, 25% hemp); gelatine.

Treatment applied: to test solubility and degree of migration of ink components through the paper, we use two different solvents for the bath: 1) water and 2) mixture of water with ethanol 20% v/v. The sample was soaked in large excess of solvent for 5 min; dried under weight (0.8g/m<sup>2</sup>) for 10 min., and finally air dried.

The instrument used was an ICP/MS (Inductively coupled plasma mass spectrometry) Perkin Elmer Elan 6000 coupled to a Brio Laser: 266 nm designed with an external optical system which allows a controlled variation of the energy irradiated (from 1 to 10 mJ) and also of the spot generated on the sample surface (from 50 to 200 microns). A newly designed ablation cell was tested for this specific application.

## 3. Results and discussion.

ICP/MS is an important atomic spectroscopic technique capable to provide isotopic information that requires sampling and dissolution of the material prior to analysis. Some years ago, a Laser Ablation system was coupled to these instruments LA-ICP/MS to allow the direct ablation of the sample avoiding, in this way, sampling and sample pre-treatment. The size of the cell of these instruments restricts its application to artwork analysis (3-5). LA-gf-ICP/MS system includes a new cell system that permits the analysis of any artwork without size restriction.

Ablation cell is made of glass with a quartz window and it is softly fixed onto the surface of the artwork by magnets. Cell allows the irradiation of the artwork and it is connected to the ICP/MS by a constant flux of Argon who brings the ablated material to the ICP (Figure 1). Successive laser pulses on the same place permits to ablate successive stratus of material that are analyzed providing the stratigraphical elemental composition.

Capability of the instrument has been first evaluated by the analysis of easel painting of known composition. The results show that the ablation produce a crater of 100 µm diameter and the resolution in



depth is around 2 and 5  $\mu\text{m}$  depending on the painting technique (oil or tempera). The information provided by LA-gf-ICP/MS agrees the actual composition of the painting and the information obtained by Scanning Electron Microscopy.

Once the capability for painting has been studied next the work is centred on the evaluation of its potential application to the study of manuscripts. This study is now in progress and it is focused on the analysis of the consequences of application of aqueous treatment to the manuscripts.

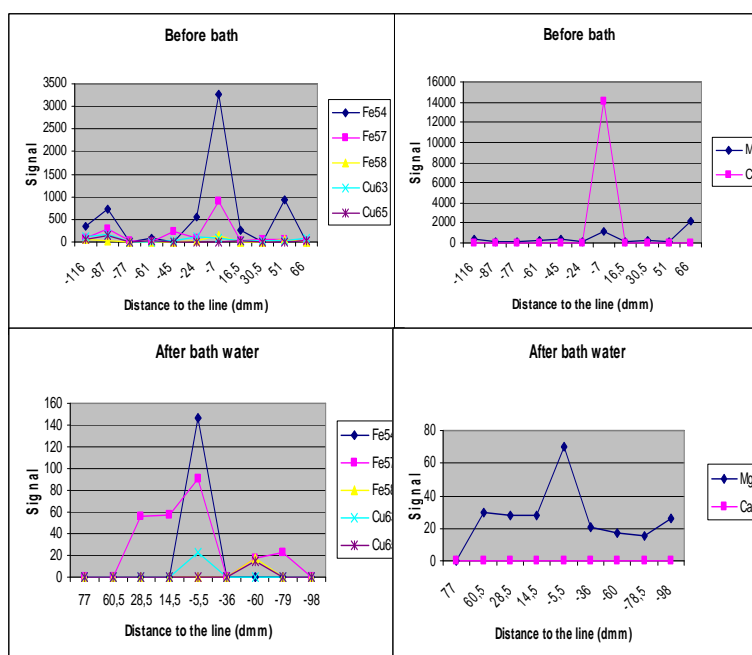
In Figure 2 it can be observed, under magnification, the state of manuscript fragment M98 after bath application and analysis by LA-gf-ICP/MS. The experimental includes 3 lines with 9 points analyzed each before bath and the same number after treatment application. First, it can be deduced that deterioration is minimum because only part of the spots can be observed.



The isotopes monitored across the surface in order to get information about ink and paper composition were Fe-54, Fe-57, Fe-58, Cu-63, Cu-65 Ca-44 and Mg-22. Figure 3 shows the distribution of signal obtained for the different isotopes. It is clear the signal decrease in the ink line and in the paper as consequence of the treatment application. It can also be observed that it appears some Fe and Cu distributed along paper surface.

However an important problem appears in the interpretation of these data in spite of the important differences observed: it is not evaluated the influence of the matrix in the values of the signals obtained for the different scenarios: ink and paper, and before and after aqueous treatment.

Nowadays, the study is trying to evaluate- calibrate the influence of these scenarios by using manuscript "instrumentum" and following two different strategies: - calibration by using standards and matrix conditioner and - signal comparison by total signal integration. (Results will be available at the workshop).



#### 4. Conclusions

Analysis of easel painting without artwork size restriction is possible by using LA-gf-ICP/MS. The application of this technique yields elemental information along stratigraphy with minimum deterioration of the pieces.

Preliminary application of LA-gf-ICP/MS to manuscript study is also promising because signals obtained for the most representative elements are significative, the spatial resolution is good enough to face problems related to manuscript treatments and the deterioration produced as consequence of the analysis is minimum.

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#### 5. References

1. B. Reissland, "Ink Corrosion-The Side Effects Caused by Aqueous Treatments for Paper Objects", in: A.J.Brown (eds), Iron GALL Ink Meeting, 4-5 September 2000, Postprints, University of Northumbria, Newcastle, 2001, 109-E. 114.
2. E. Eusman, "Effects of aqueous treatment on iron Gall Ink- Monitoring iron Migration with the Iron (II) Indicator Test, in H.K. Stratis, B. Salvesen (Eds.), The Broad Spectrum: Studies in the Materials, Techniques and conservation of colour on Pape, Archetype Publication Ltd, London, 2002, 122-127.
3. Käkkänen, H.; Houni, J.; Kaski, S. Korppi-Tommola, J.E.I. Analysis of paper by laser-induced plasma spectroscopy. *Spectrochimica Acta*, vol.562001. pp. 737-742.
4. Selih, V.S.; Strlic, M.; Kolar, J. Pihlar, B. Quantitative approach to Laser Ablation-ICP-MS analysis of iron gall ink on paper. *congrés ljubljana*, 2008.
5. Wagner, B. Bulska, E. On the use of laser ablation inductively coupled plasma mass spectrometry for the investigation of the written heritage. *JAAS*, vol.192004. pp. 1325-1329.