LA-ICP-MS analysis of historic ink and paper

- **Soft laser ablation of historic documents**
- **Calibration standards for quantitative LA-ICP-MS analysis of ink and paper**

Introduction

More than 200 years ago, the most commonly used writing ink in the Western World was an iron-gall ink, evident today in surviving manuscripts and drawings, including those by Leonardo da Vinci, Galileo, Rembrandt and many others.

Some of these historic documents are now suffering terrible damage, caused by breakdown of the paper, apparently accelerated by iron, impurity elements and other constituents in the ink. It has been found that Cu impurities in the iron sulfate, used in most ink preparations, is particularly damaging. To select the correct conservation strategy for such documents, it is essential to know the ink and paper compositions with respect to iron, copper and other transition elements.

Fig 1. Many historic documents contain iron-gall ink

Aims of controlled low-power ablation

LA-ICP-MS yields sensitive elemental analysis. In the analysis of historic artifacts, discernible ablation marks on the analyzed area need to be avoided. Such “soft” ablation is achieved by the UP213 system, using optical attenuation of the beam output, as illustrated in Figure 2.

The aim of this work is to obtain quantitative LA-ICP-MS analysis of ink and paper by soft ablation sampling, requiring the preparation of synthetic paper analytical standards of known Group (II) and transition element content.

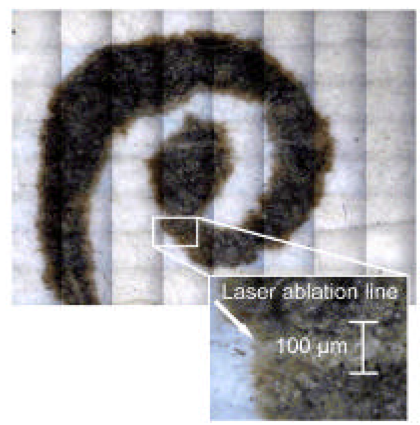

Fig 2. “Soft” laser ablation line of the UP 213 laser.

Preparing the synthetic calibration standards

The synthetic paper standards, to be used for laser ablation calibrations, were prepared from purified cellulose paper (Whatman No. 1 filter paper, Maidstone, UK). Metals were introduced to the paper by immersion into a distilled water solution of 11 analytical grade metal chlorides (Mg, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, Sr, and Cd).

The immersing solution of highest concentration contained 10 g/L of each metal salt and a sequence of diluted solutions was used for four other preparations. After a 2-minute immersion, each of the five paper samples was air-dried. The actual concentration of each metal in each paper was determined by solution ICP-MS analysis, following digestion.

Analyzing the prepared synthetic standards

The final compositions of the paper standards were determined accurately after complete digestion of samples of each paper. Approximately 50 mg of each proposed paper standard was microwave-digested in HNO_3 / H_2O_2, yielding a clear, particle free solution.[1] Each of the five papers was sampled and analyzed in triplicate and the same digestion procedure was also used on five replicates of pure Whatman paper, used for blank determination.

Instrumentation

New Wave UP213 laser system

Ablation gas: He at 0.95 L/min
Plasma make-up gas: Ar at 0.75 l/min
Crater diameter: 100 µm
Scan speed: 25 µm/s
Repetition rate: 10 Hz
Energy density: 0.1 J/cm^2

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LA-ICP-MS calibration

Having determined the composition of all five standards, they were then used to calibrate LA-ICP-MS response. Each standard (5 mm x 7 mm) was mounted onto a microscopic glass slide with self-adhesive tape. Six consecutive replicate acquisitions of each calibration sample and the blank were measured and ^{13}C was used as an internal standard.

LA-ICP-MS calibrations show that there is excellent correlation between LA-ICP-MS signal and the composition of the standard paper. All 11 elements yielded linear calibration plots of this general pattern.

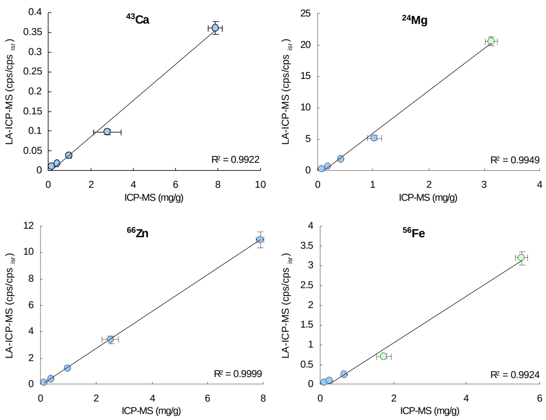

Fig 3. Calibration graphs for Ca, Mg, Zn and Fe.

Analysis of an unknown sample

The calibration standards were then used in LA-ICP-MS analysis of an 18th Century document and of a laboratory model document. The model document's ink was made using a known 18th Century formulation.

The laboratory model paper was the same cellulose paper used to prepare the standard papers, with no sizing used. The analysis summary, in Table 1, shows that the historic ink contains significant minor element impurities that do not occur in the newly formulated ink. The historic ink was only required to have good colour and adhesion to the paper. Ingredients available at that time were clearly not high in purity.

Element content [mg/g]	Original document from 18th century		Laboratory model document	
	paper	ink line	paper	ink line
Mg	0.61 ± 0.09	**4.3 ± 0.7**	0.13 ± 0.05	0.13 ± 0.02
Ca	0.7 ± 0.2	**5.0 ± 2**	0.46 ± 0.03	0.44 ± 0.04
Ti	< 0.05	< 0.05	< 0.05	< 0.05
Mn	0.21 ± 0.06	**0.4 ± 0.1**	0.18 ± 0.02	0.32 ± 0.05
Fe	0.30 ± 0.09	**39 ± 10**	0.23 ± 0.06	**1.4 ± 0.2**
Co	0.19 ± 0.06	0.20 ± 0.08	0.19 ± 0.08	0.19 ± 0.03
Ni	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
Cu	0.3 ± 0.1	0.35 ± 0.09	0.26 ± 0.03	0.36 ± 0.05
Zn	0.08 ± 0.04	**7 ± 2**	0.05 ± 0.02	0.07 ± 0.03
Sr	0.24 ± 0.06	0.28 ± 0.09	0.24 ± 0.07	0.24 ± 0.03
Cd	< 0.05	< 0.05	< 0.05	< 0.05

Table 1: Comparison of original document and laboratory model. Significant levels in inks are shown in bold.

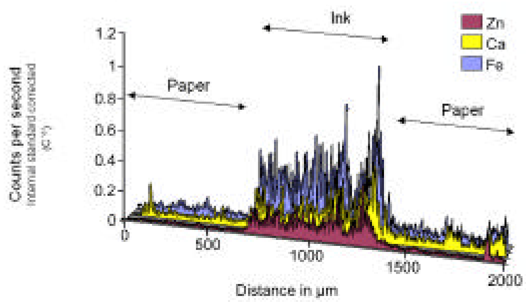

Fig 4. Laser traverse along ink line

Figure 4 shows Fe, Zn and Ca signals during a traverse across an ink line. Even though the UP 213 generates a barely discernible ablation track, the minor element content of the ink can be clearly differentiated from that of the paper.

Conclusions

Excellent LA-ICP-MS calibrations have been achieved for 11 elements using synthetic paper calibration standards.

An 18th Century iron-based ink has been shown to contain significant levels of Zn, Mn, Ca and Mg. A modern ink, made from higher purity compounds, has fewer such concomitant elements.

Using very low laser energy density, ablations tracks were only visible using a microscope.

Acknowledgment

Vid Simon Šelih
University of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia.

References

(1) Milestone application note DG-CH-07.

NEW WAVE RESEARCH
www.new-wave.com

USA
New Wave Research, Inc
48660 Kato Road
Fremont CA 94538-7339
Tel: 510-249-1550
Tel: 800-566-1743
Fax: 510-249-1551
Email: Lasers@new-wave.com

Japan
New Wave Research, KK
5F Chojiya Building, 1-36-4,
Shinjuku-ku, Shinjuku
Tokyo, 160-0022 Japan
Tel: +81-3-3351-0131
Fax: +81-3-3351-0121
Email: NewWaveKK@new-wave.com

Taiwan
New Wave Research G. C. Co., Ltd.
2Fl., No. 58-3, Xing Shan Road,
Neihu Dist., Taipei
Taiwan 114
Tel: 886-2-8792-7585
Fax: 886-2-8792-7584
Email: NewWaveCG@new-wave.com

Europe
New Wave Research Co. Ltd.
8 Avro Court
Ermine Business Park
Huntingdon, Cambridge
PE29 6XS, UK
Tel: 44-(0)1480 456 566
Fax: 44-(0)1480 456 545
Email: NewWaveEU@new-wave.com

China
New Wave Research (China) Co., Ltd
Rm. 1102, 11/F, Jiaxing Mansion,
No.877, Dongfang Rd.
Shanghai 200122, China
Tel: 86-21-5058-7785
Fax: 86-21– 5058-7786
Email: NewWaveCN@new-wave.com