Multivariate Analysis and Chemometrics applied to Environment and Cultural Heritage, Nemi (RM), 2-4 October 2006, Italy, Europe

The Use of Energy Dispersive X-ray Diffraction (EDXD) for the Investigation of the Structural and Compositional Features of Old and Modern Papers

P. Ballirano[1], **R. Caminiti**[2], **C. Sadun**[2], **G. Caracciolo**[2]

[1]Dip.to di Scienze della Terra, Università di Roma "La Sapienza", Rome, Italy.
[2]Dip.to di Chimica, Università di Roma "La Sapienza", Rome, Italy.

Abstract

This work reports the first application of the Energy Dispersive X-ray Diffraction (EDXD) for the investigation of the structural and compositional features of old and modern papers. Based on the differences observed among various types of paper and building an appropriate database we expect to be able to rapidly identify the provenance of the paper itself using a fast non-destructive technique. This result is quite interesting in the field of art conservation and archaeometry.

Introduction

The application of several experimental techniques to objects of both historical and artistic value has recently attracted a great deal of attention. In the next future, the combination of older techniques and new advances is expected to provide results in the overall field of art conservation and archaeometry [1], also the use of Multivariate Analysis can aid the study of ancient artifacts.

Among the spectroscopic techniques employed for the investigation of various art works X-ray diffraction (XRD) represents a powerful non-destructive technique that is able to provide information regarding the molecular packing of atoms and molecules inside the sample at microscopic and self-assembled levels. In the case of parchments or ancient papers, the structure of the samples has possibly undergone deterioration due to external factors.

Many samples of artistic and historical interest may also be characterized and authenticated from their elemental composition. Structural and compositional features of all mentioned samples may be simultaneously obtained by Energy Dispersive X-ray Diffraction (EDXD).

In this work, we report our first EDXD measurements carried out on paper of different provenience and age. In order to evaluate the applicability of the technique to the structural and compositional studies of paper samples, five old books were selected and the experimental findings were compared to those extracted for a modern high performance paper used for photocopies, laser and ink-jet printers.

Materials & Methods

X-Ray Diffraction experiments were carried out by an EDXD apparatus elsewhere described in detail [2]. The diffracted intensity is measured as a function of the transfer momentum q ($q = cost * E * sin$? ? $cost$ = 1.01354 $Å^{-1} * keV^{-1}$). After a preliminary set of measurements, the scattering angle of ? = 5° was selected to investigate a q-range comprises between 1 and 4 $Å^{-1}$ covering the relevant reflections of cellulose. The uncertainty associated to ? is ? ? = 0.001° and it directly affects the uncertainty ? q associated to the transfer momentum.

Results

Fig. 1 shows six EDXD patterns of paper samples of different provenience and age. All the EDXD scans contain the relevant peaks of the crystalline form of cellulose. In particular a doublet centred at q = 1.46 and 1.6 $Å^{-1}$, corresponding to the 021 and 002 reflections of cellulose, is clearly evident in all patterns while a less pronounced peak, at q = 2.43 $Å^{-1}$, is indexed as the cellulose 004 reflection. Within the investigated *q*-range, another broad diffraction peak, located at q ~ 2.1 $Å^{-1}$, is commonly found in some samples. It can be indexed as the 104 peak of calcite, i.e. calcium carbonate. The presence of the latter peak is usually explained as the result of the reaction between the calcium hydroxide retained in the paper and carbon dioxide. Comparison of the EDXD scan of different paper samples shows remarkable differences. The variation of the relative diffraction intensity between the 021 and 002 reflections of cellulose may be attributed to texture enhancement. In addition, the peak of calcite of the modern paper is very narrow and stronger than that detected in old paper. indicating that the Ca percentage in the modern paper is higher than that of old paper samples.

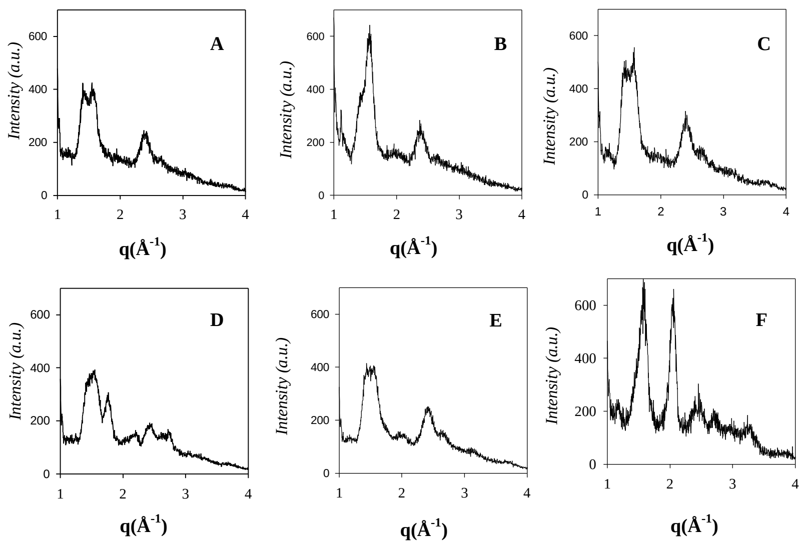

Fig. 1. EDXD patterns of old paper of different provenience and age: Firenze, Italy (1865) (A); Nashville, USA (1876) (B); Braunschweig, Germany (1888) (C); Leipzig, Germany (1913) (D); Berkeley, USA (1951) (E); Fabriano, Italy (2004) (F).

In all the investigated samples traces of Fe are evident arising from iron oxide, whereas traces of Pb and Cr, detected in the sample labelled as B, are possibly due to the presence of traces of $PbCrO_4$–based ink [3]. Modern paper shows a very low percentage of Fe with respect to older paper and a much higher Ca content in agreement to the discussed features of the diffraction pattern of Fig. 1 (labelled as F).

Conclusions

In this paper EDXD was applied, for the first time, to the structural and compositional characterization of old and modern paper samples. These preliminary results confirm that EDXD is a suitable and efficient method for this kind of investigations. In the next future, systematic structural investigations are expected to clarify technological aspects of early papermaking and also broaden our basic knowledge about paper performance in general.

References

1) L. R. Ember, Chemistry serves art, *Chem. Eng. News,* 79 (2001) 51-59
2) R. Caminiti and V. Rossi Albertini, Review on the kinetics of phase transitions observed by energy dispersive X-ray diffraction, *Int. Rev. Phys. Chem.*, 18 (1999) 263-299.
3) J. L. Ferrero, C. Roldan, D. Juanes, J. Carballo, J. Perire, M. Ardid, J. L. Lluch, R. Vives, Study of inks on paper engravings using portable EDXRF spectrometry, *Nuc. Instr. and Meth. Phys. Res. B*, 213 (2004) 729-734.