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Abstract

Paper can be produced from various raw materials, which give rise to differences in the permanence and durability of the paper product. Modern paper is characterised by a tendency to discolor and become brittle, both problems being generally related to the high acidity of these papers. In order to avoid the loss of historical paper documents to this discoloration and embrittlement, many approaches have been developed to deacidify the high acid papers. However, there is a problem to verify the effectiveness of the different strategies. For this work a synchrotron X-ray microprobe was used to study the distributions of elements, related to the deacidification treatments, within papers treated with specific processes. These elemental distributions can serve as indicators of the effectiveness of each individual process. The microprobe is located at beamline X-26A at the Brookhaven National Laboratory, National Synchrotron Light Source and utilised a 7×10 μm^2 collimated beam of X-rays from the synchrotron. Scans were performed transverse to paper sections to obtain elemental distribution through the sample. Some preliminary results of measurements on treated and untreated paper samples are presented.

1. Introduction

The use of microanalytical techniques in the field of conservation of cultural property is very common, because the study of the degradation processes and the control of the effectiveness of the treatments frequently requires a microanalysis. Therefore, a considerable body of microanalytical techniques are actually used in the field of the paper conservation, some of these are non destructive. In the last decade several techniques have been used to study the microscopic distribution of elements across the surfaces of manuscripts with Raman [1], proton [2] and photon [3] microprobes. Those studies demonstrated the use of microanalytical techniques for the identification of inks and pigments in ancient manuscripts. Harbottle et al. [4], described the design and the sensitivity of an X-ray microprobe and discussed assets and limitations of such a facility for use in conservation. An X-ray microprobe is a more sensible analytical system than an electron microprobe, having in addition the advantage to allow the non destructive study of object of art in air. This can be actually done also with a proton beam but with several limitations [5]. The non destructivity is not relevant for the application presented in this paper.

Paper can be produced from various raw materials which can result in substantial variabilities in their permanence and durability. Many modern papers are characterised with a relatively high acid content which can lead to discoloration and embrittlement and ultimately the complete loss of the document. Similar problems have been reported because of the acid content of certain inks. These acid problems have led to the development of several techniques for the treatment of the papers in order to deacidify them on a large production scale. However, at this moment, none of the proposed techniques is totally well accepted. In order to determine the acceptability of any particular technique, the effectiveness of the different treatment strategies needs to be verified.

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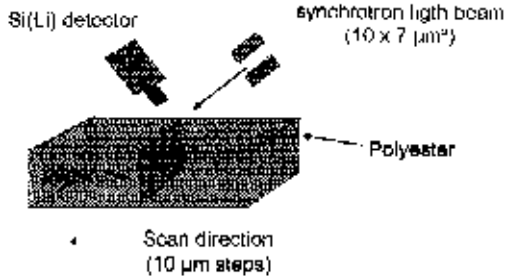

Fig. 1. Sketch of the paper sample encapsulated in the polyester resin. The arrow shows the scan direction.

In 1990 the Library of Congress published specifications for deacidification processes [6]. The specifications state that uniformity for a given paper type shall vary from specified optimal concentrations by no more than ±20% between books, and by no more than ±20% between and within individual pages. Because the acidity is distributed throughout the paper, part of these specifications include certifying the uniformity of the alkaline treatment material on the surface and inside the paper. Therefore it is important to determine that the active elements used for deacidifying the papers are also distributed throughout the paper.

A measurement of the elemental concentration only through the surface of a paper sample is inadequate since it provides no distribution information of the elements in the thickness of the sheet. The active elements may be contained on the surface and not distributed throughout, and especially inside, the paper. Therefore a technique such as a microprobe is needed to measure the active element distributions across a cross section of the paper.

In this article we report some preliminary measurements of distributions of some key processing elements (magnesium, calcium, and zinc) within papers that have undergone certain stages of deacidification processes. The measurements were made using a synchrotron X-ray microprobe.

2. Materials and methods

Several pieces of ancient and modern papers, supplied by Stazione Sperimentale Cellulosa e Carta (Italy), have been used for these analyses. The set of papers:

(1) woodpulp with neutral gluing 166 μm thick.

(2) Kraft white pine, neutral gluing, thickness 112 μm;

(3) Linters, neutral gluing, thickness 131 μm.

A fourth set consisted of B-CTMP (Aspen River), 1% amid, 1% aluminium polichlorure was supplied by Cartiere Fuvini, Rossano Veneto, Italy. Finally, a fifth set included several pieces of an ancient manuscript (1829) which

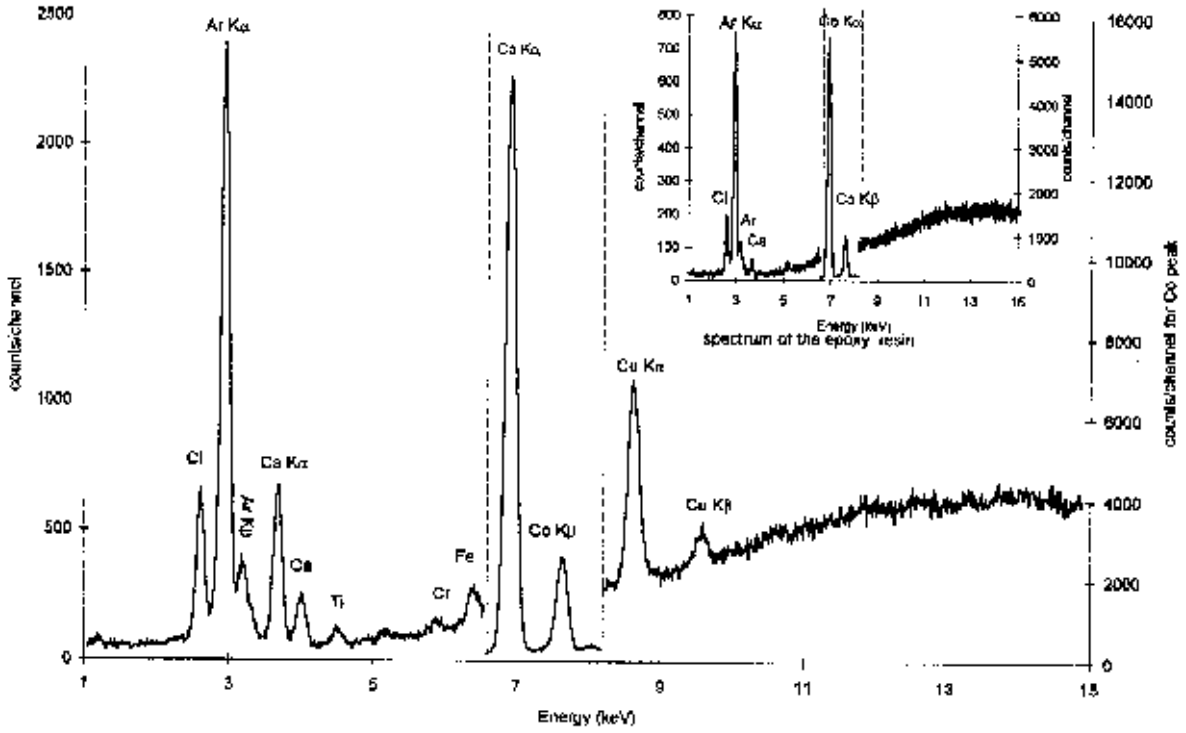

Fig. 2. X-ray spectrum of the central part of a 166 μm thick paper made with woodpulp with neutral gluing (sample 1). Unfortunately, the presence of the cobalt K-peaks, demonstrates a diffusion of the polyester resin into the paper.

needed to be deacidified. The pieces of the manuscript were:

(5a) no treatment;

(5b) washed with tap water;

(5c) treated with calcium hydroxide in a half saturated water solution;

(5d) treated with a 3% calcium acetate in 10% H_2O and 90% CH_3OH solution.

The pieces where carefully encapsulated in polyester resin and then cut. In this manner measurements could be performed on a transversal section of the paper sample (see Fig. 1). Some of the measurements were performed in inked portions of the paper to determine if the ink affects the distribution of the active elements.

The measurements were done at the National Synchrotron Light Source, beam line X-26A located at Brookhaven National Laboratory. The experimental apparatus is similar to that described previously for X-26C [7]. The main difference is that the sample on X-26A is 9 m from the source instead of 20 m. The samples were mounted at 45° to the beam on a stepping motor driven X–Y–Z–θ sample stage with minimum step size of 1 μm in X–Y–Z and 0.001 degree in θ. The "white light" (directly from the synchrotron, filtered only with four Be windows) X-ray beam was collimated to 7×10 μm^2 with the beam centred on the mid-plane of the synchrotron. The fluorescence spectra were measured with a 30 mm^2 Si(Li) detector mounted at 90° to the incident X-ray beam. This detector has an energy resolution of 150 eV at 5.9 keV. No filters were used on the detector to avoid attenuation of the calcium X-rays. The sample position was monitored with a microscope equipped with a video camera. The relative intensity of the incident X-ray beam was determined with a helium filled ionization chamber located after the collimators. The spectra were acquired for approximately 1 to 2 min and the scans had dwell times of approximately 10 s.

3. Results

The measurements reported here are preliminary. We tested the capability of the X-ray microprobe to perform the measurements needed in analysing the effectiveness of paper deacidification processes. Fig. 2 is a spectrum of the woodpulp paper sample (1) having the pattern of low concentration elements, such as calcium, titanium and iron, typical of a modern paper. The presence of the calcium, titanium, iron, copper and zinc peaks demonstrates the possibility to detect these elements with short measuring times (10 s). Unfortunately, the presence of the cobalt

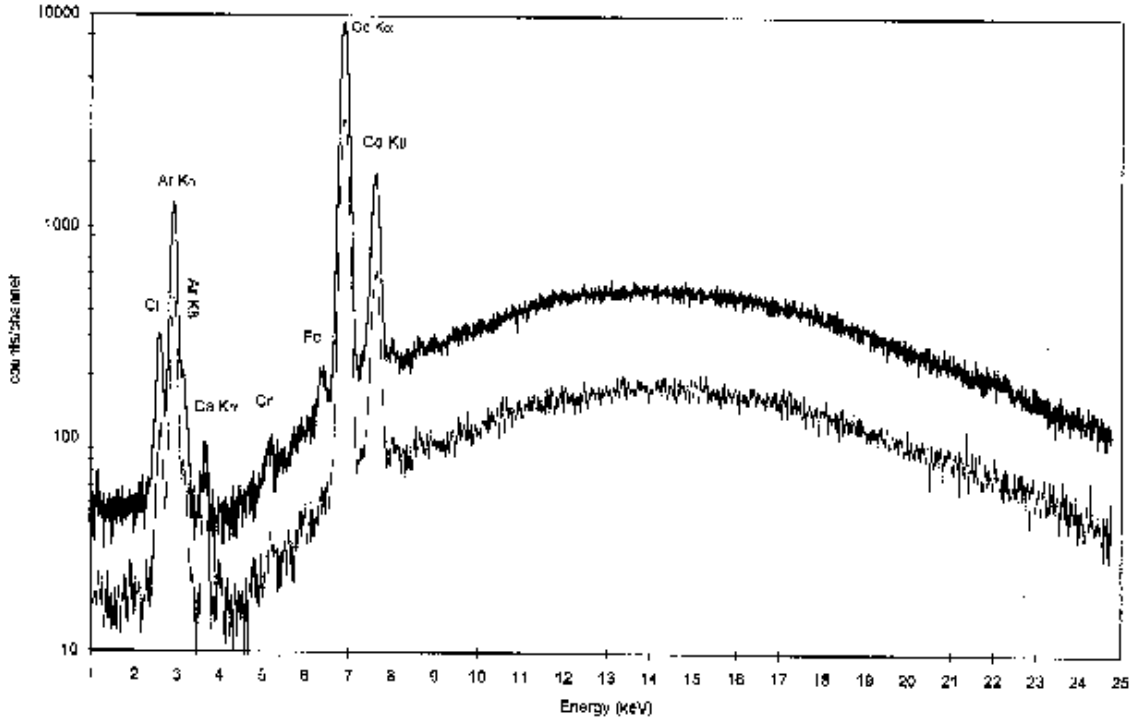

Fig. 3. X-ray spectra of the polyester resin. Cobalt is the catalyst used for the polymerisation of the resin.

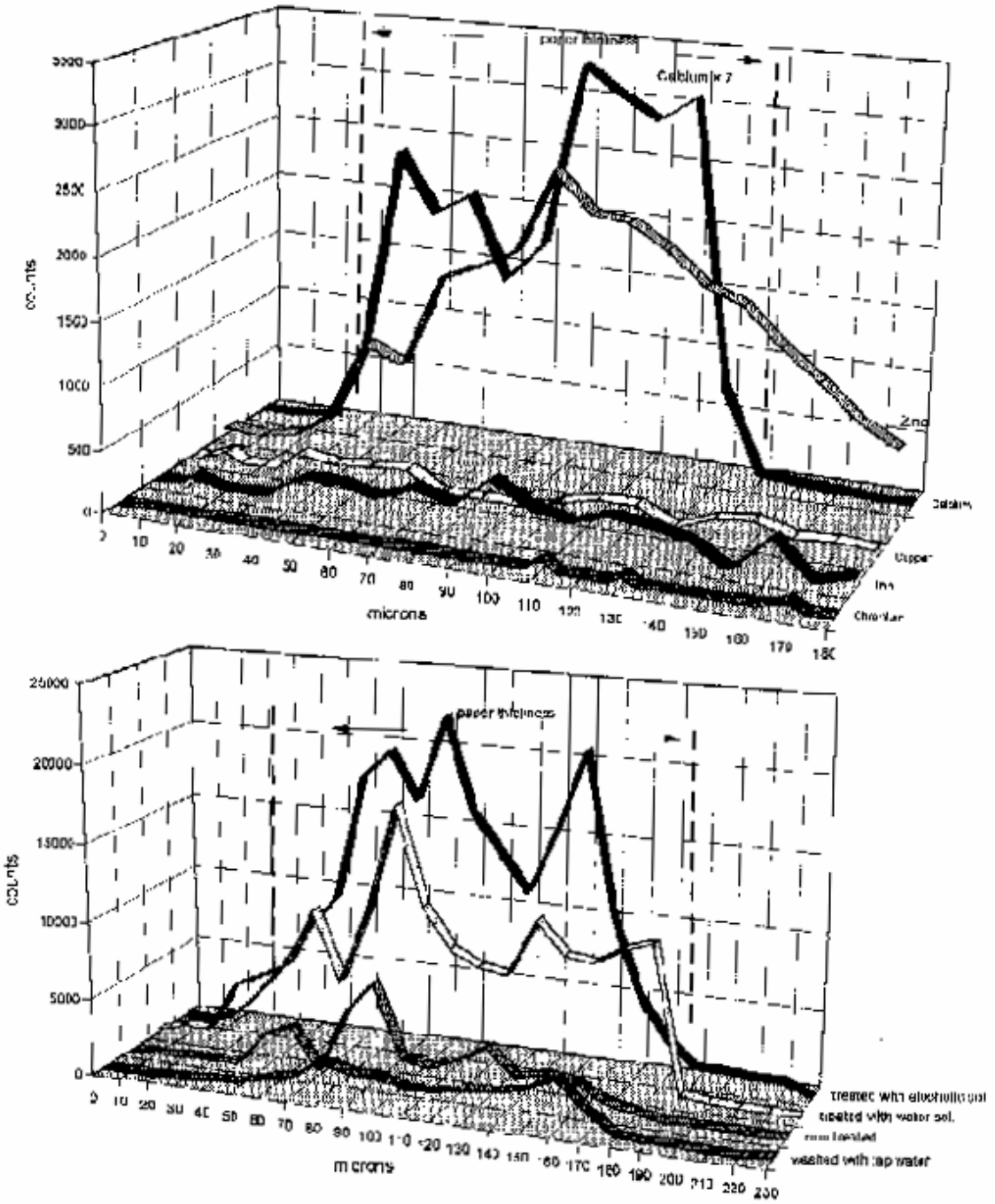

Fig. 5. Calcium profiles within samples of a manuscript paper, untreated, washed with tap water, deacidified with a calcium hydroxide water solution and with a calcium acetate diocholic solution.

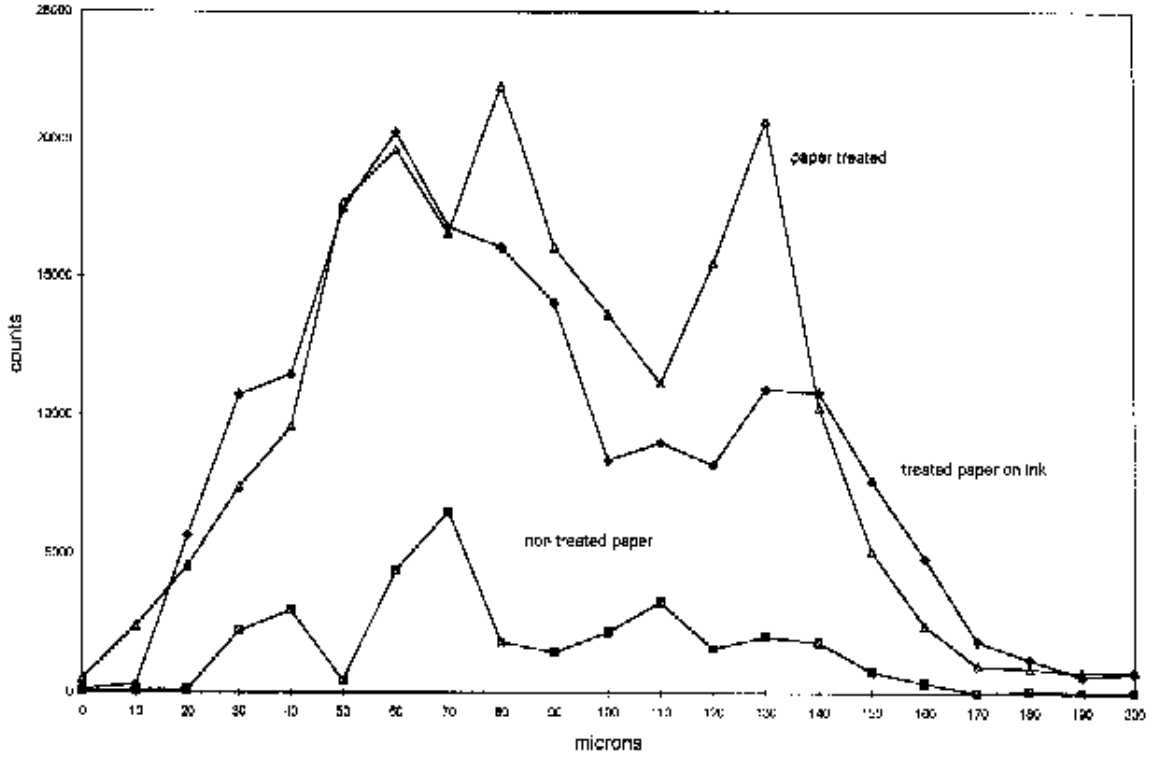

Fig. 6. Calcium profiles within samples of a manuscript paper, not treated paper, paper treated with a calcium acetate alcoholic solution with and without the presence of ink.

K-peaks (due to the resin catalyst), demonstrates a diffusion of the polyester resin into the paper; in Fig. 3 a spectrum of the resin is shown. It is possible that this polyester diffusion could itself cause a rearrangement of the elements of interest in the paper, so these results should be considered as strictly a demonstration of principle. Fig. 4 shows the results of a scan on paper number (2), as described above. It is possible to observe from the calcium and zinc distribution that the paper thickness is approximately 113 μm, a value consistent with independent previous measurements (thickness tester).

Fig. 5 shows the calcium distributions within paper number (5) for the 4 treatment stages mentioned above. Significant fluctuations in the calcium concentrations can be easily observed. These fluctuations, related to a non-uniform distribution of the calcium in the paper, can probably be due to different causes. In the case of the paper treated with water solution the point-to-point fluctuations are approximately 30%. In the case of the treatment with alcoholic solution the point-to-point fluctuations in calcium concentrations are approximately 20%. This, together with the higher calcium concentration, could be a demonstration that the alcohol solution helps the calcium to diffuse and equilibrate throughout the paper [8,9].

There is a question as to whether the presence of ink can influence the deacidification process by inhibiting the diffusion of the active elements into the paper. Fig. 6 shows scans for calcium with and without the presence of ink. These data demonstrate the calcium being able to diffuse into the inked area of the paper so the treatment processes can be effective in the presence of ink.

4. Conclusions

There are many questions regarding the deacidification or other restoration processes of papers where the knowledge of spatial distributions of elements in the paper could be of interest. The high sensitivity of the synchrotron X-ray microprobe and possibility of obtaining 10 μm spatial resolution elemental distributions is extremely useful to understand the conservation processes. The measurements of elemental distributions along a cross section of the paper sample tells us if the active elements have diffused sufficiently into the interior of the paper to neutralise the acid levels throughout the paper. Efficient treatment of the paper is important since too little treatment could leave the paper in an acidic state or with non-uniformities. The spatial resolution, 10 μm, available with the synchrotron microprobe, is appropriate for these samples whose thickness varies from 110 to 160 μm.

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