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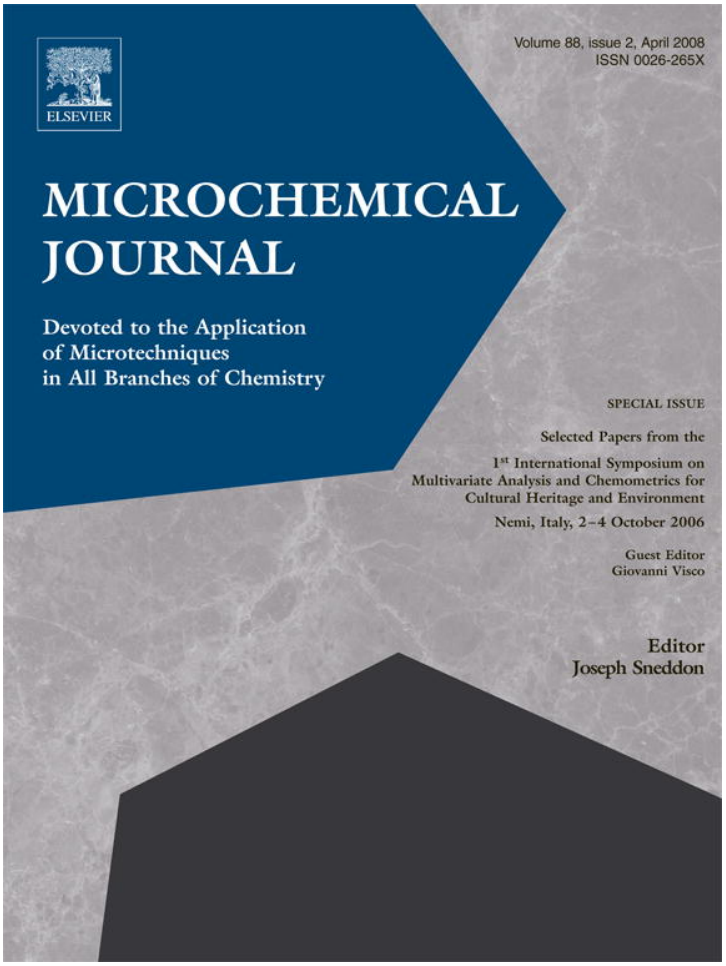

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The use of energy dispersive X-ray diffraction (EDXD) for the investigation of the structural and compositional features of old and modern papers

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Abstract

This work reports the first application of the energy dispersive X-ray diffraction (EDXD) for the characterization of old and modern papers. Based on structural and compositional 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 promising in the field of art conservation and archaeometry.
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1. Introduction

The application of several new experimental techniques to characterize objects of both historical and artistic value has recently attracted a great deal of attention due to the large amount of information for both public and scientific benefit. In the next future, the combination of old but well established and new promising techniques is expected to provide results in the overall field of art conservation and archaeometry [1].

Among the spectroscopic techniques employed for the investigation of various art works, those based on X-ray radiation provide the opportunity to carry out analyses without sample damaging. Different kinds of X-ray analyses may be used such as X-ray diffraction (XRD) [2], X-ray fluorescence (XRF) [3], particle induced X-ray emission (PIXE) [4] and X-ray photoelectron spectroscopy (XPS) [5]. Although it may be necessary to use a combination of several techniques to obtain a complete characterization of the sample, XRD represents a powerful non-destructive technique providing information on the structural features of the samples at the atomic level. In the case of parchments or ancient papers, the structure of the samples may have suffered from additional deterioration due to external factors. Collagen deterioration at the molecular level results in the breakage of covalent bonds leading to an increased molecular disorder [6]. Moreover, XRD provides information on the organization of single collagen molecules into fibrils and fibres. Different fibres produce distinct X-ray diffraction patterns as a function of the deterioration state providing a unique opportunity to detect the corresponding structural changes. Discrete changes of the periodicity of collagen arrangement, as well as variations of the degree of cristallinity, may be easily detected by XRD [6]. Recently, XRD has been also applied to the investigation of the relationship existing between the mechanical properties and the structure of wood at the nanometric level [7].

In this emerging field of research, XRD analyses have rendered possible a series of non-destructive preliminary investigations on parchments and books to be conserved or restored, thus improving the basic knowledge of these materials. These studies should represent the first step for many planned intervention on handmade object.

Many samples of artistical and historical interest may also be characterized and authenticated from their elemental composition. For example, some artists may have used specific paints containing particular compounds. If these components may be

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detected, then the piece could be traced to a certain artist or time frame. Moreover, with historical samples, it may be essential to understand the elemental composition of the piece to find a means to prevent further decomposition for conservation purposes. XRF provides analysis of the sample bulk composition. A compositional analysis can be performed since these X-rays are typical of the atoms from which they fluoresce. This elemental analysis is non-destructive and requires at least 50 μm or 0.5 mg of sample [8].

Structural and compositional features may be simultaneously extracted from energy dispersive X-ray diffraction (EDXD) experiments. This non-conventional diffractive technique has been generally used for the structural investigation of samples characterized by a short-range order [9]. Therefore, all systems of artistical and historical value with a low degree of cristallinity may potentially be studied by EDXD. Moreover, recent works on inorganic materials and on biological systems of medical interest have demonstrated its applicability also to fully crystalline systems [10,11]. In principle, EDXD is a powerful tool characterized by the above mentioned advantages typical of the spectroscopic techniques. It is completely non-destructive and it allows the simultaneous collection of XRD and XRF data therefore providing information on both structural and compositional features of the sample. Finally, the acquisition times are sensibly shorter than those typical of any other in-house apparatus being of the order of seconds [12]. In this work, we report our first EDXD measurements carried out on papers of different provenance and age. In order to evaluate the applicability of the technique to the structural and compositional studies of paper samples, seven books (of age spanning from 1766 to 1951, see Table 1) 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.

2. Experimental

X-Ray diffraction experiments were carried out by an EDXD apparatus elsewhere described in detail [12]. Here we briefly report the principal features of the instrument. A collimated polychromatic X-ray radiation produced by a standard W sealed-tube, operating at 55 kV and 45 mA, is used and the diffracted beam is energy resolved by a solid state detector located at a suitable scattering angle θ. The diffractometer operates in vertical θ/θ geometry and is equipped with an EG&G solid-state liquid-nitrogen-cooled ultrapure Ge detector characterized by a resolution of 120 eV at 5.9 keV. Both X-ray tube and detector can rotate around the centre of the goniometer where the sample is placed. The diffracted intensity is measured as a function of the transferred momentum q ($q = \text{cost}^{*}E^{*}\sin\theta$; $\text{cost} = 1.01354$ Å^{-1} * keV^{-1}). A photograph of the diffractometer is given in Fig. 1. After a preliminary set of measurements, scattering angles of $\theta = 4$, 5, and 10° were selected to investigate an overall transferred momentum range $1 < q < 10$ Å^{-1}, covering the relevant reflections of cellulose. With respect to traditional diffractive techniques, EDXD is characterized by several advantages: (a) measurements do not depend on the intensity fluctuation of the primary beam; (b) the diffractometer is static during data acquisition reducing the errors due to misalignment; (c) the time of measurement is strongly reduced with respect to traditional angular dispersive techniques. In the present study the collection time for each EDXD scan was of 100 s.

Table 1
List of the analysed samples

Year	Provenance	Title/paper type	Author
1766	Paris, France	Dictionnaire de chemie, Tome Premier	T.J. Macquer
1831	Venezia, Italy	Trattato di chimica Tome II Parte II	G.J. Berzelius
1865	Firenze, Italy	Lezioni elementary di chimica organica	R. Piria
1876	Nashville, USA	Tables for systematic qualitative chemical analysis	J.H. Snively
1888	Braunschweig, Germany	Zur Erinnerung an for Angegangene Freunde	A.W. von Hoffmann
1913	Leipzig, Germany	Abhandlungen und Forträge zur Geschichte der Naturwissenschaften	E.O. von Lippmann
1951	Berkeley, USA	The California wine industry: a study of the formative years	V.P. Carosso
2004	Fabriano, Italy	Cartiere Miliani S.p.A. Copy 2 Performance	–

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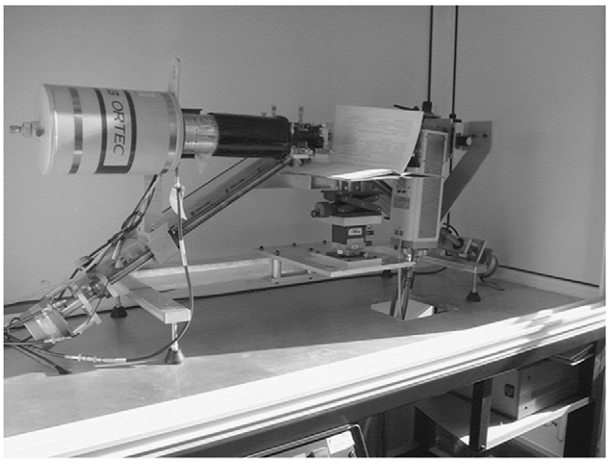

Fig. 1. Photograph of the energy dispersive X-Ray diffractometer. The investigated samples are directly posed at the optical centre of the diffractometer.

3. Results and discussion

Fig. 2 shows the EDXD patterns of two old books (Dictionnare de Chimie and Trattato di Chimica, see Table 1) collected at $\theta = 4$ and 10°. For comparative purposes the diffraction patterns of natural cellulose and lignine, collected with a fully-automated parallel-beam X-ray powder diffractometer Siemens D5005, operating in Debye–Scherrer geometry, using CuKα radiation are reported at the centre of the panel (2θ range 13–60°). Insets show the common $2 < q < 4$ Å^{-1} range. It is clear that the pattern measured in EDXD at $\theta = 10°$ shows many additional diffraction effects not experimentally accessibly by a conventional instrument or in EDXD at $\theta = 4°$. This fact may provide additional information for sample identification and

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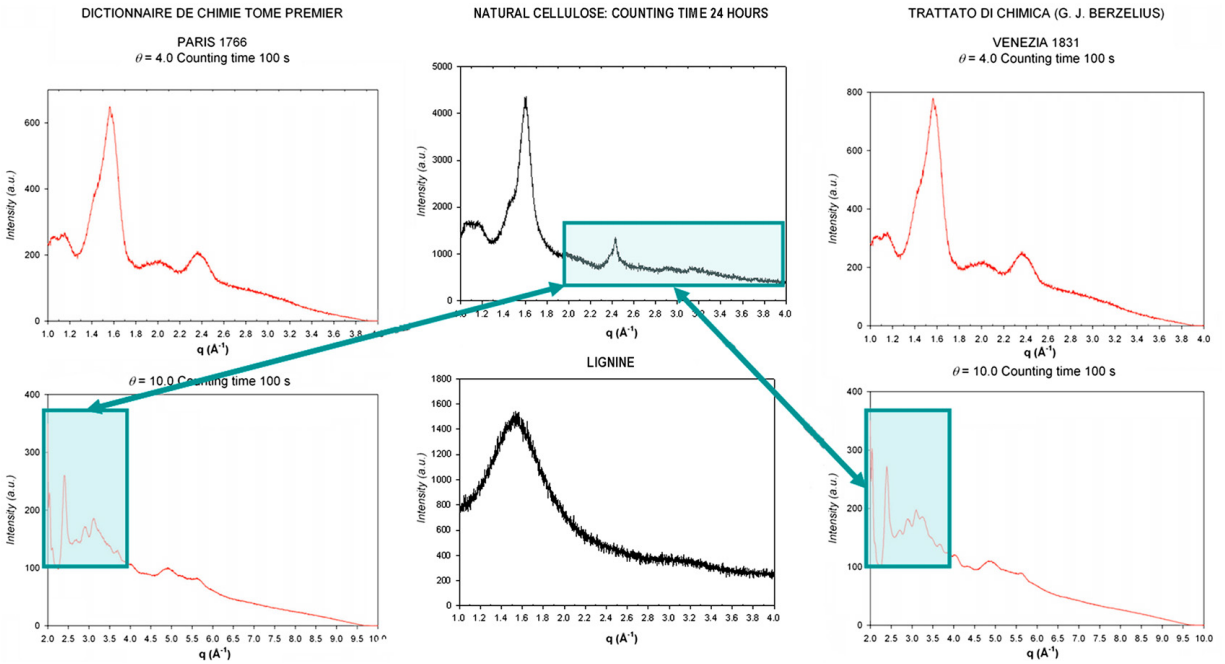

Fig. 2. EDXD patterns of two old papers. At the centre X-ray powder diffraction patterns of natural cellulose and lignine collected on a Siemens D5005 equipped with Goebel mirror on the incident beam and Peltier-cooled Si(Li) solid-state detector. Sample prepared as capillary. See text for explanation.

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characterization. It is also clear that both papers consist of native cellulose. In fact, native cellulose is a mixture of two different crystalline polymorphs named cellulose I_α [13] and I_β [14]. On the contrary, cellulose II [15] is the stable crystalline form obtained by regeneration or mercerization of cellulose I. The calculated diffraction patterns of the three polymorphs are reported in Fig. 3 (calculated from structural data [13–15]). As can be easily seen the discrimination between cellulose I_α and I_β is not trivial whereas polymorph II is characterized by a quite different diffraction pattern. In fact, differences between the two I polymorphs are barely visible as additional weak effects in the $2<q<3.5$ Å^{-1} range. Relevant peaks for both I polymorphs (Fig. 3a,b) are two doublets centred at $q=1.06$ and 1.16 Å^{-1} and at $q=1.46$ (shoulder) and 1.59 Å^{-1}, as well as a less pronounced, broad peak, at q ca. 2.40 Å^{-1}. Polymorph II (Fig. 3c) is characterized by a peak at $q=0.95$ Å^{-1} and a well resolved doublet at $q=1.40$ and 1.55 Å^{-1}.

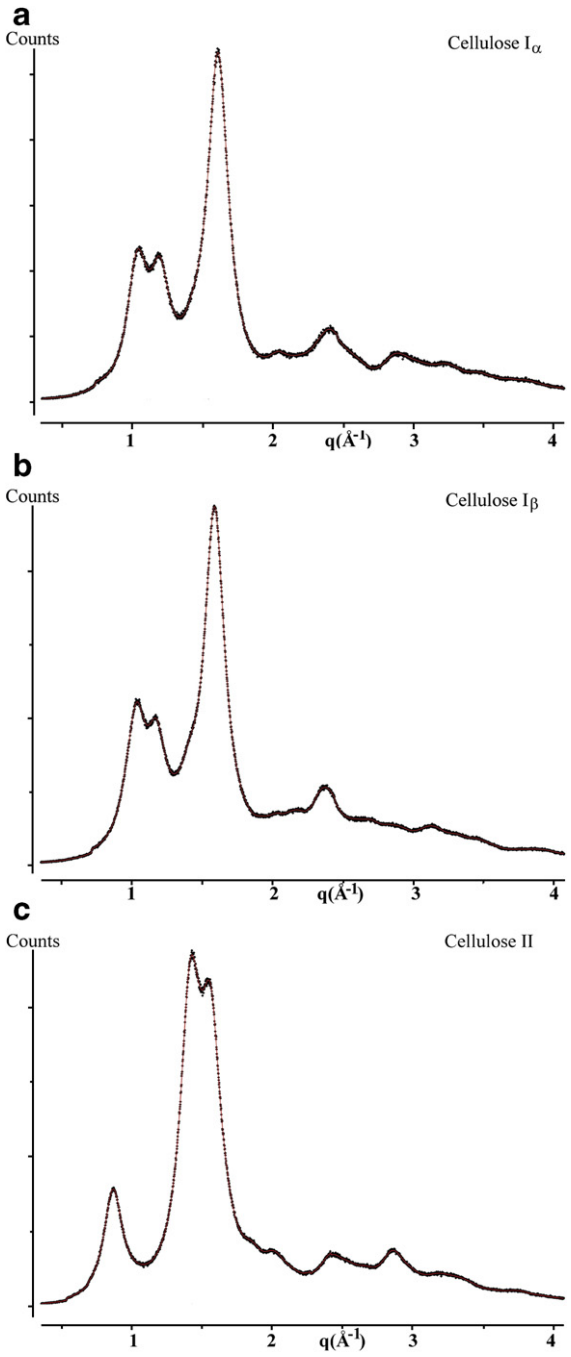

Fig. 3. Calculated X-ray powder diffraction data of a) cellulose I_α; b) cellulose I_β; c) cellulose II. Structural data are those of reference [13–15]. Calculations carried out with the crystallographic package GSAS (Larson and Von Dreele, 2000).

According to its amorphous features the presence of lignine cannot be detected in the diffraction patterns of paper.

Fig. 4 shows six EDXD patterns of paper samples of different provenience and age (see Table 1). All EDXD scans contain the relevant peaks of the crystalline forms of cellulose. In the case of the book from Leipzig (1913) the 101, 102 and 110 reflections of $KAl(SO_4)_2$, arising from sizing treatment, have been detected. Within the investigated q-range, another strong diffraction peak (as well as less intense others), located at $q\sim2.1$ Å^{-1}, has been found in the diffraction pattern of the modern paper. It is indexed as the 104 peak of calcite, i.e. calcium carbonate. The presence of calcite is related to its use as filler.

Comparison of the various diffraction patterns shows that there are differences with respect to the cellulose polymorphic composition of the samples, as can be seen from the magnified $1.2<q<1.9$ Å^{-1} range of the corresponding EDXD patterns (Fig. 5). In fact, the paper of the books from Firenze (1865), Braunschweig (1888), Leipzig (1913), and Berkeley (1951) contain the polymorphic form II of cellulose whereas the remaining retain the original polymorphic form I (α and/or β) of native cellulose. Such differences are clearly related to different papermaking technologies. Such behaviour has been reproduced by treating natural cellulose with NaOH [16,17].

By collecting a full EDXD pattern ranging from the small angle X-ray scattering (SAXS) to the wide angle X-ray scattering (WAXS) region we could build the structure function of each sample in order to obtain information about the precise atomic structure of each sample [10]. Anyway, since showing the applicability of EDXD to this intriguing and emerging field of research is the main goal of the present communication, we did not focused on the calculation of the overall structure function of the analysed samples. Here we want to stress that just observing the modulation of the intensity of the spectra is sufficient to conclude that each sample shows proper structural and packing properties at the atomic level. At least in principle systematic EDXD analyses could reveal alterations of the structural organization of cellulose due to deterioration factors such as fire, humidity or pollution levels.

In Fig. 6 we report the energy dispersive X-Ray fluorescence (EDXF) spectra of the same six samples of Fig. 4. In our spectra, the W fluorescence L-lines of the X-ray source as well as the fluorescence lines of the elements composing the sample are simply superimposed to the diffraction pattern and a unique measurement is therefore required. In all the investigated samples traces of Fe are evident. Traces of Pb and Cr have also been detected in the sample from Nashville (1876), possibly due to the presence of traces of $PbCrO_4$-based ink [18].

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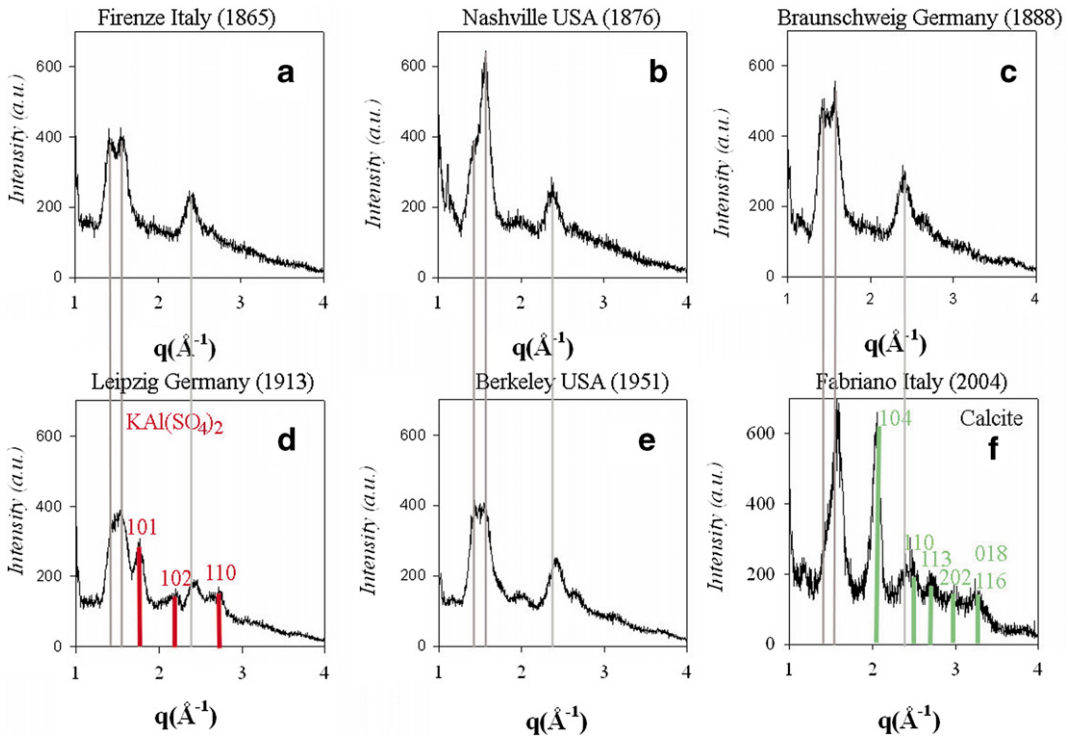

Fig. 4. EDXD patterns of old paper of different provenance and age: Firenze, Italy (1865) (a); Nashville, USA (1876) (b); Braunschweig, Germany (1888) (c); Leipzig, Germany (1913) (d); Berkeley, USA (1951) (e); Fabriano, Italy (2004) (f).

On the contrary the sample of 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. 4 (labelled as f). These compositional differences are directly interpretable in terms of the different papermaking technologies [19].

4. Conclusion

In this paper EDXD was applied, for the first time, to the simultaneous structural and compositional characterization of some samples of old and modern papers. Preliminary results confirm that EDXD is a suitable and efficient method for this kind of investigations. In the near future, systematic structural investigations are expected to clarify technological aspects of early papermaking and also broaden our basic knowledge about paper performance in general. Evaluation *via* multivariate analysis of such structural information for a large number of samples may eventually led to the definition of cellulose structure/papermaking/ageing relationships. In particular using a larger number of samples, decomposition of diffraction patterns into their components (i.e. cellulose polymorphs I and

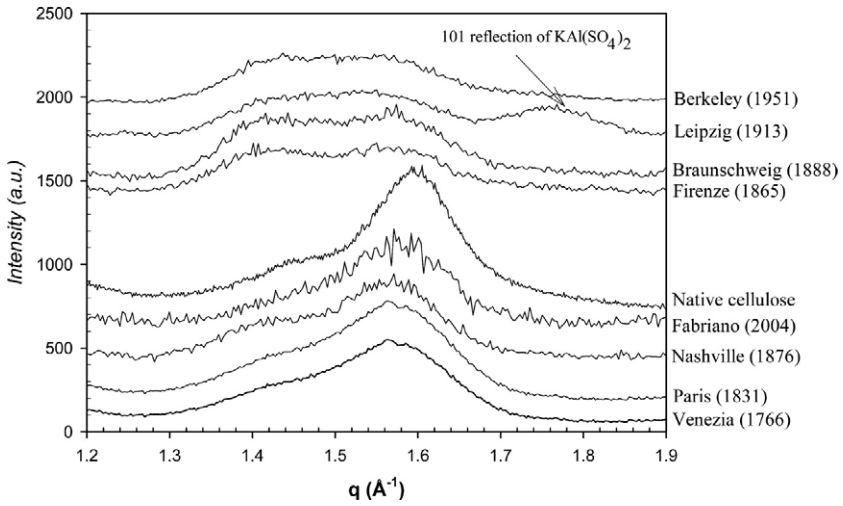

Fig. 5. Magnified view of the $1.2 < q < 1.9$ Å^{-1} range.

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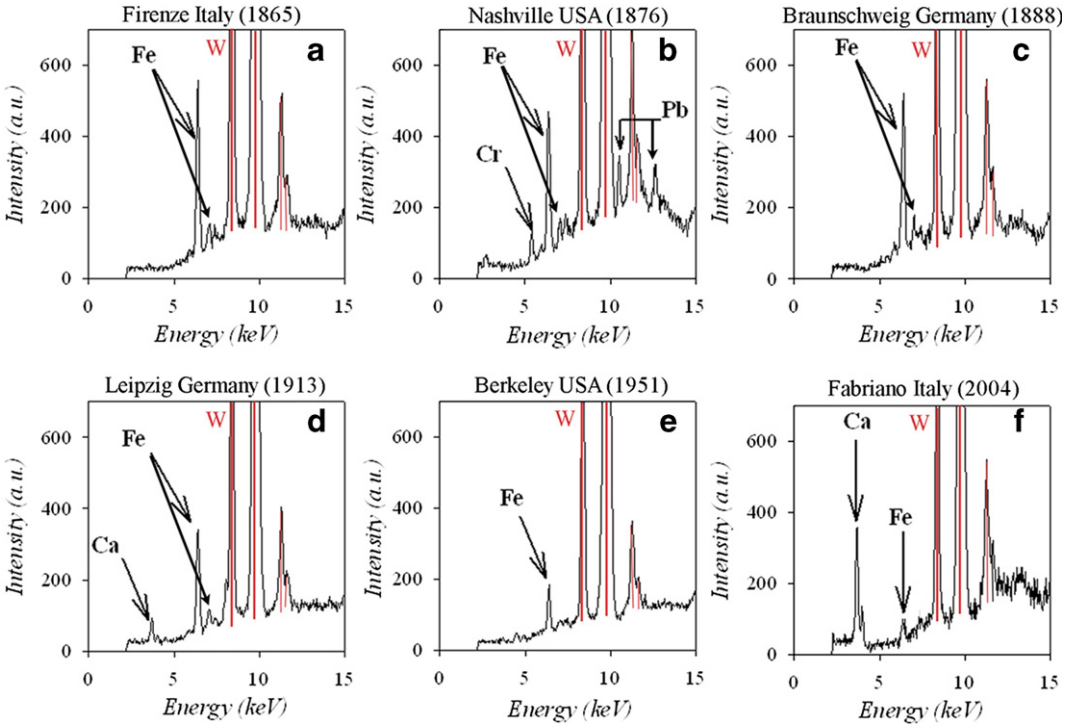

Fig. 6. EDXF spectra of the investigated samples. Red vertical bars refer to the W fluorescence line from the X-ray source target. Each pattern has been collected for $t = 10$ s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

II) could be carried out by curve resolution techniques *via* opportunely designed constraints. Multivariate curve resolution [20] is expected to provide good results due to its flexibility and wide applicability.

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