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Identification of cellulose ethers in cultural heritage by means of MALDI-TOF-MS.

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KEYWORDS: Cellulose ethers, MALDI-TOF-MS, FTIR, NMR.

ABSTRACT: Cellulose ethers used as adhesives in heritage conservation treatments have been successfully identified by means of MALDI-TOF-MS, a technique non-previously applied for this purpose in cultural assets. This is of relevant importance for long-term conservation, as discrimination among the diverse types of cellulose ethers that may have been applied to an asset during conservation treatments is essential in order to guarantee stability of artworks. The proposed method also allows discrimination among these adhesives spread on paper-based artworks, where cellulose ethers have been extensively utilized for many years, overcoming interferences usually occurred due to the cellulosic nature of both adhesive and support. Successful results have been obtained from mock ups and small samples of paper-based original artworks with usual low concentrations of adhesive. FTIR and NMR have been used as complementary analytical techniques.

RESEARCH AIMS

This research pursues the identification of cellulose ethers in heritage assets. On the one hand, this article intends to provide a method for the identification of the most commonly used cellulose ethers used nowadays or in the past in heritage conservation: CMC, EC, EHEC, HEC, HPC, MC, MHEC, MHPC. The method must be feasible to be performed in cultural assets. So, identification has to be feasible taking into consideration conservation guidelines and standards for sampling cultural assets. Besides, the method must be useful in the low concentrations usually encountered in heritage assets. Due to the wide use of cellulose ethers in conservation treatments of paper-based assets, the method ought to be suitable to identify the different types of cellulose ethers impregnated on paper supports, avoiding interferences caused by the similar nature of both materials in small and low concentrations when using other methods and techniques described in the literature hitherto.

1. INTRODUCTION

Adhesives are present in cultural heritage either as original materials or as compounds added during conservation treatments. Their characterization is of extreme importance for broad knowledge and conservation of heritage assets. Adhesives used along the years in these pieces are usually classified by its origin into natural, artificial and synthetic [1]. Natural adhesives are commonly divided into proteinaceous and vegetable-based substances. Both date back from ancient times and have remained relevant in conservation treatments to the present day. These adhesives are easily identified by spot tests or Fourier transform infrared spectroscopy (FTIR). Discrimination among different proteins or their diverse origin and sources has been performed by analysis of deoxyribonucleic acid (DNA) [2] and immunology techniques [3], peptide mass mapping [4], high performance liquid chromatography coupled with electrospray ionization mass spectrometry (HPLC-ESI-MS) [5], matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) [6] or principal component analysis (PCA)

[7]. Characterization of different gums or mucilages is commonly performed by chromatographic techniques and electrophoresis [8]. Identification of dextrin or starch origin, manufacture process of these materials and paste preparation methods has been carried out by X-ray crystallography [9] and optical microscopy [10, 11]. More recently starch ethers started to be evaluated for conservation purposes [12, 13, 14] and identification has been performed in other fields by FTIR, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and X-ray crystallography [15] and pyrolysis gas chromatography mass spectrometry (Py-GC-MS) [16]. Artificially and synthetically produced adhesives appeared in the 19th and 20th century and have been used in heritage conservation treatments from the second half of the 20th century. Synthetic polymers are commonly identified by FTIR, Py-GC-MS, direct temperature-resolved mass spectrometry (DTMS) [17], or nuclear magnetic resonance (NMR) [18]. Cellulose derivated adhesives - cellulose esters and ethers- are the most important artificially produced adhesives used in cultural heritage. Cellulose esters are no longer advised for conservation treatments. Identification have been successfully conducted by using FTIR with PCA [19], by analyzing its volatile organic components (VOC) emissions with thermal desorption-gas chromatography coupled with mass spectrometry (TD-GC-MS) [20] or by near-infrared hyperspectral imaging [21]. Conversely, cellulose ethers are very used nowadays by conservators either alone or in combination with starch and/or acrylic emulsions, in order to, among other possible reasons, acquire longer working times, modify viscosity or rheological properties, flexibility or penetration into supports [11, 22-26].

In general, cellulose ethers are water-soluble polymers with a cellulose backbone and ether containing substituents. They are produced by the chemical modification of cellulose with concentrated sodium hydroxide followed by reaction with one or more etherifying agents such as methyl chloride, ethyl chloride, ethylene oxide or propylene oxide.

Ethers of cellulose were first synthesized by Wilhelm Suida in 1905 [27], but it was not until the 1920s that these were commercialized in Germany [28]. By the 1930s cellulose ethers were already available in the United States and after World War II they became well established [29]. From 1960 it is easy to find references of its use for conservation of graphic works [30-32] and other cultural assets [33, 34]. The different types of cellulose ethers have been very frequently used in treatments of paper-based artworks and documents from the last decades of the 20th century onwards [22-26, 35-40].

Identification of cellulose ethers in cultural heritage is of critical importance since some types commonly used in the past are not stable in the long term. From 1970 much work was done on the evaluation of these adhesives for conservation [41] and over the years, further research has been developed in this topic. Some studies indicate that some types of Methyl Cellulose (MC), Hydroxy Methyl Propyl Cellulose (HPMC), and Carboxy Methyl Cellulose (CMC) show good long-term stability with negligible weight loss or discoloration after artificial ageing [29, 42, 43]. Nevertheless, these studies advise against other ethers used in the past such as Ethyl Cellulose (EC), Ethyl Hydroxy Ethyl Cellulose (EHEC) and Hydroxy Propyl Cellulose (HPC). However, other significant research found that some HPC-based adhesives artificially aged also remained stable [44, 45]. Presumably, discrepancies in the literature may be due to differences in the performed tests, possible deviations caused by diverse artificial ageing methods, or variations among all cellulose ethers available within each chemical family (chain length, manufacture processes, etc.).

Against this background, it turns out to be essential to know the type of cellulose ether present in a cultural asset. However, too often this remains unknown. For many years the type of cellulose ether was not stated in the conservation reports, where ethers appear under generic trade names without describing the specific type of cellulose ether, nor providing information about their basic characteristics and features.

Probably this was due, among other reasons, to the fact that many local distributors did not use to supply the complete information of cellulose ethers they were selling, i.e., chemical species of the ether of cellulose, manufacturer product, molecular weight, viscosity, ash content, degree of substitution, pH, mechanical properties, etc. In some countries this is still quite common nowadays.

So, it is very common to find conservation reports indicating that some kind of cellulose ether was used with no further information on the type or its properties. In these cases, analyses are needed in order to understand the possible risks in the long-term caused by the adhesive.

Despite identification of cellulose ethers by MALDI-TOF has been described before [46-48] this procedure has not been applied to the characterization of these compounds in paper-based artworks yet. Although there are several cases of characterization of cellulose ethers in cultural heritage via FTIR [49-52], wide-angle X-ray scattering (WAXD), TGA / differential thermal analysis (DTA), and differential scanning calorimetry (DSC) [53] the identification of low amounts of different types of cellulose ethers spread on cellulosic supports - with the resulting signal interference due to similar nature among adhesive and support-, has not been fully addressed yet.

Recent research reports MALDI-TOF as a successful technique in the identification of MHEC on lined modern posters [54]. Moving forward along this path, in this research a method has been developed and different types of cellulose ethers commonly used in conservation have been successfully identified by MALDI-TOF-MS even when spread on paper supports. NMR and FTIR have been employed as complementary techniques to complete the identification. Identification has been successfully achieved both in mock-ups and in original paper-based artworks or archival documents.

2. MATERIALS AND METHODS

This research focuses on the analysis and identification of eight cellulose ether types most used in conservation of cultural heritage: CMC, EC, EHEC, HEC, HPC, MC, MHEC, and MHPC. Within these typologies, twenty cellulose ethers manufactured by producers providing most conservation suppliers have been selected for analysis. The selection is listed in Table 1.

Samples of all adhesives were taken directly as provided by the manufacturer (labelled samples A) and samples of paper Whatman®#1 impregnated with prepared adhesives (labelled samples B) were performed for analysis. In samples B, adhesives were prepared according to the manufacturers indications. All cellulose ethers except Ethocel Standard 10 and Ethocel Standard 100 were prepared at 2% (weight/volume) in MilliQ water. Once powdered adhesives had been dispersed in one third of the water volume at 100ºC, the rest of the water was added as ice, at 0ºC, to reach dissolution of the adhesive. Ethocel™ Standard 10 and Ethocel Standard 100 were prepared, as indicated by the manufacturer, at 2%(weight/volume) in ethanol and in isopropanol: toluene (10:90), respectively. All the adhesives were spread on Whatman#1 papers by using the 100microns groove of a Cube Film Applicator Sheen 6SH 11030P.

The identification method has been also conducted on two historic paper-based documents.

The first document, referred to as Document 1 is the 21st page of a copy from the newspaper *La Vanguardia*, released on 17th November 1951. The support is made of mechanical-chemical pulping mixture with medium lignin content and it measures 15 in x 20.2 in size, 14µm thick, 75g/m2 grammage. It is a machine made paper without watermark. According to the conservation report, MC had been used to consolidate the margins in 2003.

The second document, referred to as Document 2, is a photomechanical reproduction of the engraving executed by German Audran (1631 - 1710) included as a frontispice in the first volume of Laurentius Beyerlinck poliantea "Magnum theatrum vitae humanae: hoc est, rerum divinarum, humanarum que syntagma catholicum, philosophicum, historicum, et dogmaticum. Ad normam polyantheae universalis dispositum", published in Lyon in 1666. The printing characteristics of this reproduction denote that it probably dates from the first half of the 20th century. The carved appearance typical of burin work in engravings has been partly lost as the reproduction was developed by etching through a light sensitised

Cellulose Ether	Commercial Adhesive
CMC	Blanose™ 7H3SF H Blanose™ 7MF
EC	Ethocel™ Standard 10 Ethocel™ Standard 100
EHEC	Bermocoll E 270FQ Bermocoll E 481FQ
HEC	Cellosize WP09H Natrosol 250GR Natrosol 250HR Natrosol 250LR Tylose H 10 YG4
HPC	Klucel E Klucel G
MC	Methocel A 15C Methocel A4C Methocel A4M
MHEC	Tylose MH 300P Alcasit N
MHPC	Methocel E4M Methocel k100M

Table 1. Commercially available cellulose ethers selected for the study.

plate. Besides, the typical variable height of the ink lines in engravings is not noticeable in this print, because acid bite produced lines of the same height in the matrix. The paper support measures 14 in x 8.7 in size, 22µm thick, 130g/m2 grammage and it consists of a laid handmade rag paper without watermark. Some conservation treatments had been carried out in this asset in 2003, including mechanical cleaning, washing, resizing and filling of losses. According to the conservation report, HPC had been used in the two latter treatments.

MALDI-TOF-MS experiments were performed using a 4800 MALDI TOF/TOF (ABSCIEX) instrument with a Nd:YAG Laser that operates at 355nm. Mass spectra were acquired in reflector mode. For all samples mass spectra were acquired in positive ion mode except for CMC that was acquired in negative ion mode.

2,5-Dihydroxybenzoic acid (DHB) was used as matrix. DHB was dissolved in a concentration of 10g/L in H_2O/MeOH (1:1, v/v) or in $CHCl_3$:CH_3CN (1:1, v/v) according to the solubility of the cellulose. The matrix and depolymerized cellulose solutions were mixed 1:1 (v/v). A portion (1µL) of the mixture was deposited on a MALDI sample plate and it was air dried previous to the analysis.

Partial depolymerization of the cellulose ethers was necessary in order to obtain material in a suitable mass range, i.e. less than 5KDa, for chemical characterization of cellulose derivatives. Acidic depolymerization was performed according to the method described in the literature [55] with some modifications.

For the A samples 10mg of the dry sample were dissolved in 1mL of aqueous trifluoroacetic acid (TFA, 2M) or in 1mL $CHCl_3$ (TFA 2M) according to the solubility of the cellulose. The solution was heated to 75ºC in an ultrasonic bath for 1h and left to cool to ambient temperature before used for MALDI analysis without further purification.

For the B samples 50µL of aqueous trifluoroacetic acid (TFA, 2M) or $CHCl_3$ (TFA 2M) according to the solubility of the cellulose, were added to a piece of $5mm^2$ of sample in an Eppendorf vial. The mixture was heated to 75ºC in an ultrasonic bath for 1h and left to cool to ambient temperature. The resulting suspension was then centrifuged (6000rpm, 2min) and the supernatant collected. The solvent was evaporated under a stream of nitrogen and the residue was redissolved in 3-5µL of MeOH or $CHCl_3$ according to the solubility of the cellulose, before used by MALDI analysis.

This method was replicated for analyzing original samples of Document 1 and Document 2.

Micro-FTIR in the transmition mode was used in order to identify CMC. Samples A did not need preparation. The adhesive was extracted from samples B as described above and was tested with an IR-Plan Spectra Tech microscope coupled with an infrared spectrometer Fourier Bomem MB-120 working from 700to 5000 cm^{-1} with a maximum 1 cm^{-1} resolution.

NMR was used in order to discriminate between MHPC and MHEC, as these were not easily distinguished with MALDI-TOF-MS in all cases. Identification of powdered MHPC and MHEC (A samples) was performed adding 20mL of chlorhidric acid 0,1M to 11mg of each cellulose ether. For analysis of B samples, 20mL of chlorhidric acid 0,1M were added to a piece of $5mm^2$ of paper impregnated with MHPC and MHEC. In both cases the preparation was kept at 25ºC for 48h. Finally, all the samples were introduced in the ultrasonic bath for 0,5h. The solutions were analyzed by NMR. The 1H NMR spectra were recorded at 25ºC in heavy water (D_2O) using a Varian INOVA 500 NMR spectrometer for the samples A and a Bruker Avance 600 NMR spectrometer for the samples B.

3. RESULTS AND DISCUSSION

In this research, different types of cellulose ethers used in cultural heritage have been identified with the proposed method.

Figure 1 show examples of MC, EC, HEC, HPC, EHEC successfully identified by MALDI-TOF-MS. In these spectra groups of signals corresponding to different units of glucose are identified with differences m/z 14Da, 28Da, 44Da, 58Da, resulting from fragmentation of substituent groups in the different types of cellulose ethers.

The proposed method is suitable to identify among these types of cellulose ethers even when these are impregnated in a cellulosic support, as it can be observed in Figure 2.

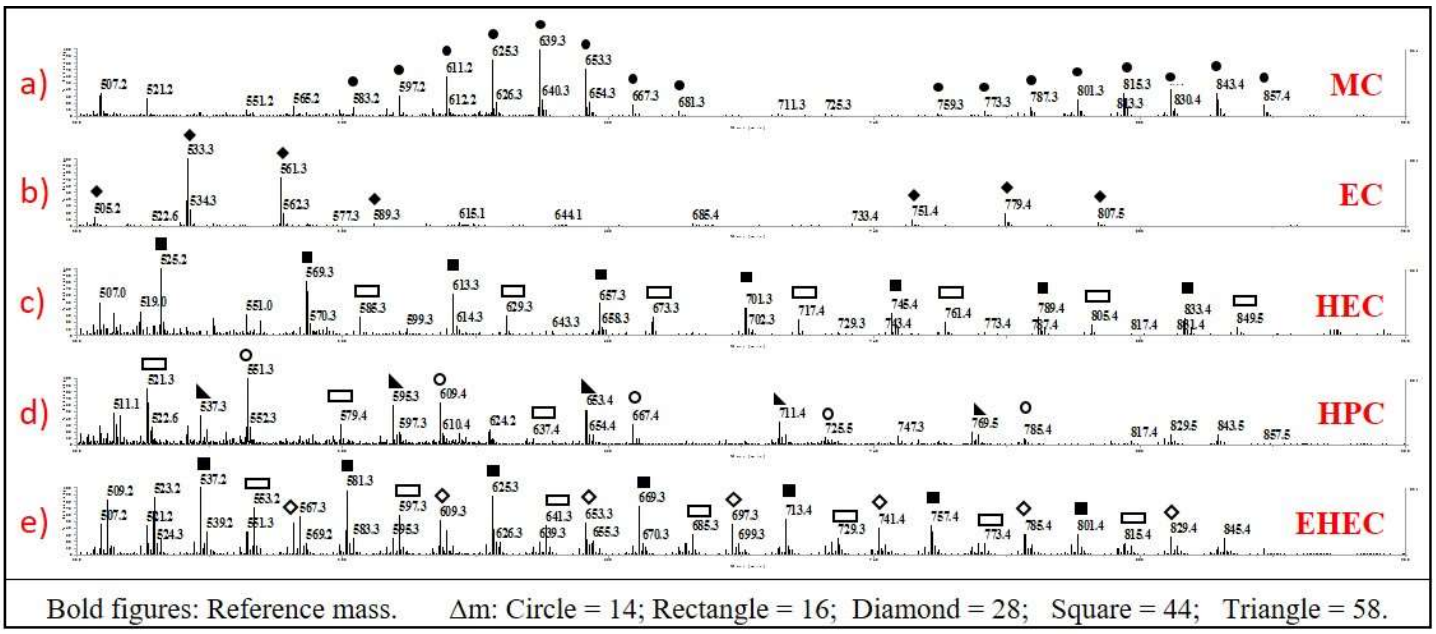

Figure 1. Examples of MALDI-TOF-MS spectra for Samples A. Mass differences pointed out in every trace confirm the nature of the cellulose ethers: **1a)** Methocel A4M (MC), Δm=14 (Methyl group); **1b)** Ethocel Standard 10 (EC), Δm=28 (Ethyl group); **1c)** Natrosol 250LR (HEC), Δm=44 (Hydroxyethyl HE group) adjacent peaks (Δm=16) confirm the presence of –OH substituent from HE; **1d)** Klucel G (HPC), Δm=58 (Hydroxypropyl HP group), adjacent peaks (Δm=16 and Δm=14) confirm the presence of –OH and Methyl substituents from HP ; **1e)** Bermocoll E 270FQ (EHEC), Δm (reference peaks)=44 (Hydroxyethyl group) adjacent peaks (Δm=16 and Δm=28) confirm the presence of –OH and Ethyl groups.

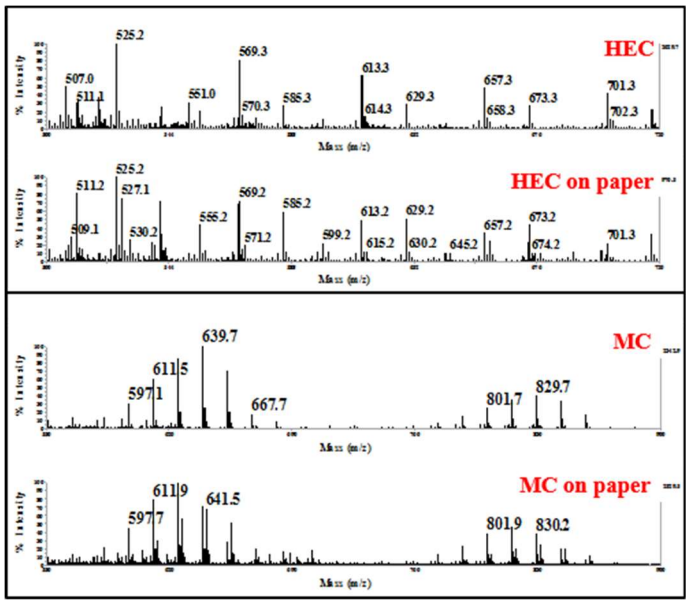

Figure 2. MALDI-TOF-MS spectra. Top: HEC adhesive Natrosol 250LR. Above: powdered adhesive (A samples). Below: adhesive impregnated in Whatman#1 paper (B samples). Bottom: MC adhesive Methocel A4M. Above: powdered adhesive (A samples). Below: adhesive impregnated in Whatman#1 paper (B samples).

In some cases characterization of CMC has not been possible with a reduced amount of sample (bellow 10mg). Detection of MHEC and MHPC is possible by MALDI-TOF-MS but it has been noted that their spectra are quite similar resulting in difficult identification (see Figure 3). Figure 4 shows a diagram with a proposed procedure for the identification in these cases.

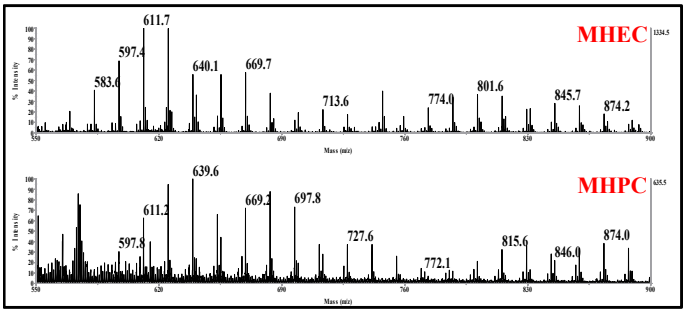

Figure 3. MALDI-TOF-MS spectra of MHEC adhesive Tylose MH 300P (above) and MHPC Methocel E4M (below).

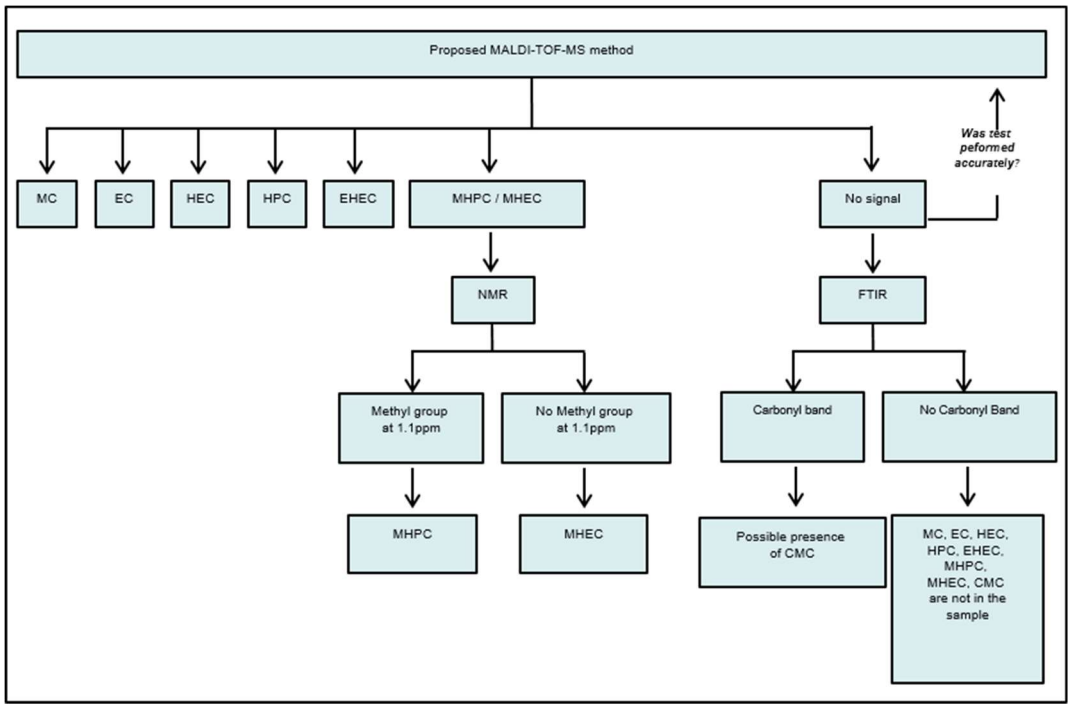

Figure 4. Proposed MALDI-TOF-MS method for the identification of cellulose ethers used in conservation treatments, even when these have been spread on paper-based supports.

FTIR analyses were performed in order to identify CMC. Absorbance of the carbonyl group has been used as an indicator of CMC because none of the other cellulose ethers used in conservation contains this substituent. The high response of this group in the infrared region allows detection of this adhesive at low concentrations.

Samples A (ground adhesive) of two different CMC were identified by FTIR (Figure 5). Carbonyl band visible at 1597cm^{-1} indicates presence of CMC in Blanose 7H3SF H and Blanose 7MF.

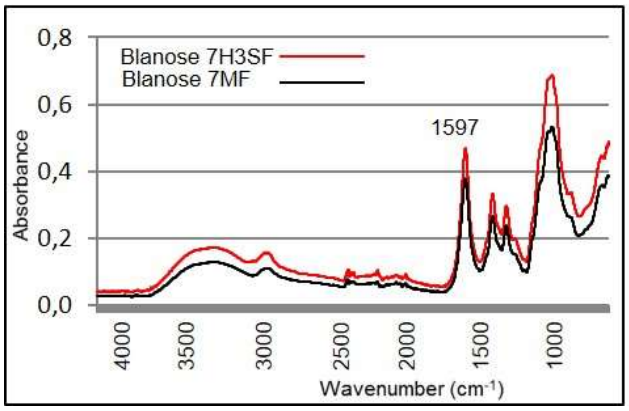

Figure 5. FTIR spectra of powdered CMC adhesive Blanose 7H3SF H and Blanose 7MF (A samples).

FTIR analysis were also performed on a selection of B samples (paper Whatman#1 impregnated with prepared adhesives). Extracts of B samples that had been prepared for MALDI-TOF-MS analyses were used to conduct FTIR in the transmission mode. In Figure 6, the carbonyl band visible at 1597cm^{-1} points out the presence of CMC in the extract of a Whatman paper impregnated of Blanose 7H3SF. In this chart, extract obtained from a Whatman paper impregnated of Methocel A4M shows the absence of response around 1600cm^{-1}, as it does not contain carbonyl groups.

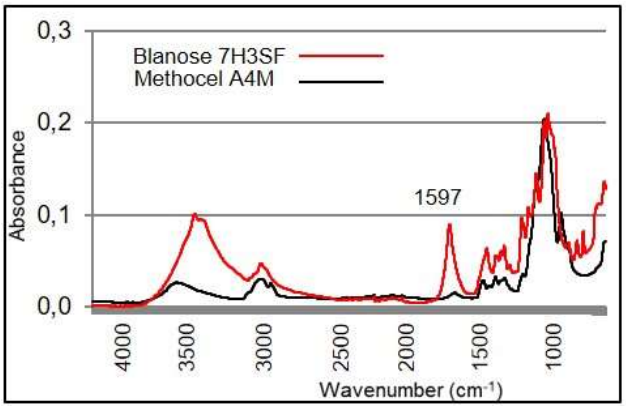

Figure 6. FTIR spectra of CMC adhesive Blanose 7H3SF and MC adhesive Methocel, both impregnated on paper (B samples).

NMR analyses have been useful in order to clearly distinguish among MHEC and MHPC. Figure 7 shows samples A (ground adhesive) NMR spectra of Tylose MH 300P and Methocel E4M that are easily differentiated. Samples B (prepared adhesives spread on cellulosic support) of these same products have been also successfully distinguished, as shown in Figure 8.

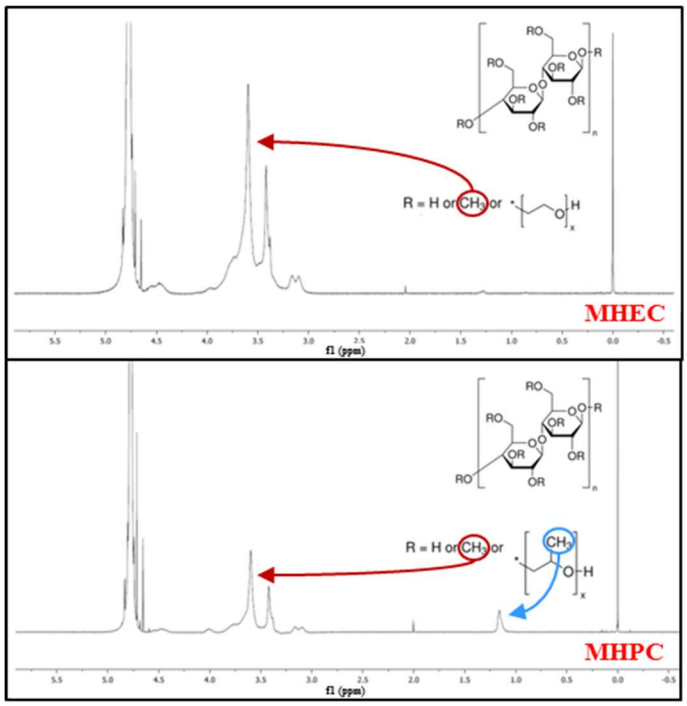

Figure 7. NMR spectra of MHEC adhesive Tylose MH 300P (above) and MHPC adhesive Methocel E4M (below).

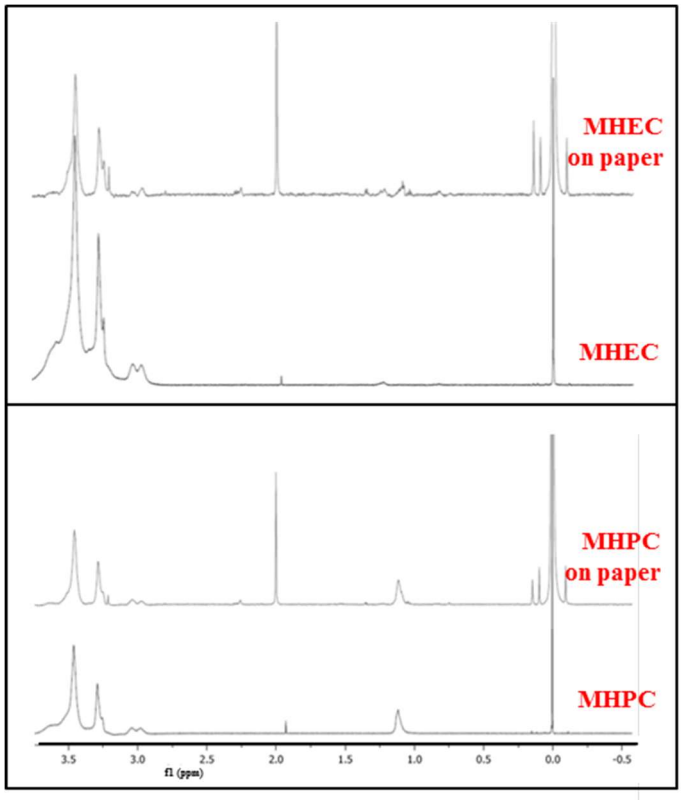

Figure 8. NMR spectra. Top: MHEC adhesive Tylose MH 300P on paper (B samples) and powdered adhesive (A samples), above and below, respectively. Bottom: MHPC adhesive Methocel E4M on paper (B samples) and powdered adhesive (A samples), above and below, respectively.

The proposed method for the identification of cellulose ethers in cultural heritage assets has been applied to two historical paper-based works, a newspaper and a chalcographic print, both from the mid-20th century. As shown in Figure 9, MC has been identified in Document 1. In Document 2 HPC was clearly characterized as it can be observed in Figure 10.

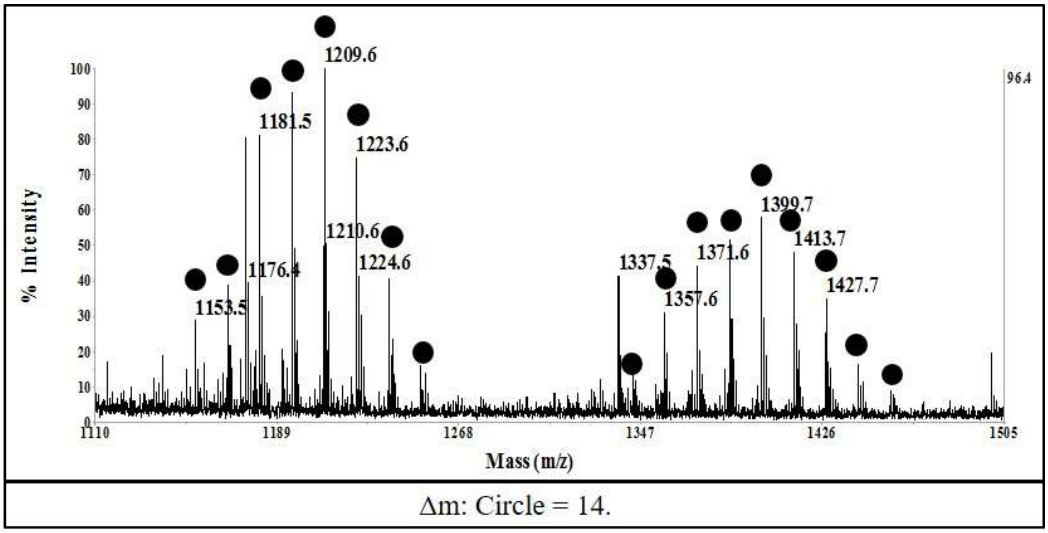

Figure 9. MC is clearly identified in Document 1. Differences of 14 Da are indicative for the presence of methyl substituents.

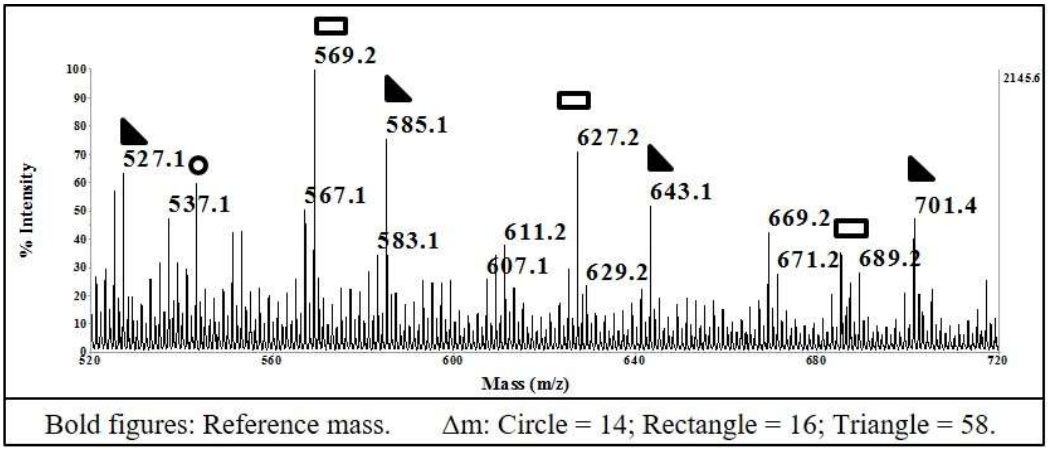

Figure 10. HPC is clearly identified in Document 2. Differences of 58 Da are indicative for the presence of hydroxypropyl substituents. Adjacent peaks (Δm=16 and Δm=14) confirm the presence of –OH and methyl substituents.

4. CONCLUSIONS

MALDI-TOF-MS has proved to be a useful technique to distinguish the majority of the cellulose ether species used nowadays or in the past in heritage conservation: CMC, EC, EHEC, HEC, HPC, MC, MHEC, and MHPC. This is of special relevance given that in the last years the use of some cellulose ethers commonly applied in the past have been discouraged for conservation purposes. The proposed method can be used to identify damaging cellulose ethers on artworks, offering the chance to undertake actions which would guarantee long-term conservation.

Although characterization of some cellulose ethers by MALDI-TOF-MS had been described before in analytical chemistry contexts, the technique had not been applied to enhance knowledge of these materials in cultural heritage before. The article describes a method to successfully discriminate the different types of cellulose ethers feasible to be performed in cultural assets with regards to standards for sampling artworks and low concentrations usually encountered in heritage objects. The method is also suitable to be performed in paper-based assets where cellulose ethers have been impregnated into the support. The proposed procedure allows extraction of cellulose ethers from small samples of paper with low concentrations of these adhesives avoiding cellulose residues. This physical separation prior to conducting analysis provides concise results circumventing interferences caused by the similar nature of both materials in small and low concentrations when using other methods and techniques described in the literature hitherto. This is especially important in view of the wide use of cellulose ethers in conservation treatments of paper-based artworks where the type of cellulose ether applied in the past remains unknown and therefore, the long-term conservation is currently uncertain.

5. FUNDING

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