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INNOVATIVE METHODS OF ANALYSIS AND DIAGNOSIS OF NATURAL AND SYNTHETIC POLYMERIC MATERIALS

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Abstract: *The study of natural and synthetic polymeric materials from modern and contemporary textile artworks can give scientists some difficulties in identification of the fibers or other components. Sometimes, time or environmental conditions can damage quite enough textile articles and because of that more and more techniques have been developed in order to assess the need to a better analysis of the samples. In addition to the lack of analytical equipment that can sometimes appear, a big problem is also the interpretation of the results. The main advantage of modern and contemporary textiles is that these products are easier to analyze because the time and environmental conditions at which they were exposed to do not have yet a major impact on them. In this paper are presented several types of analyzes and equipment that have non-destructive or micro-destructive properties. Some of these techniques have been used for decades, while others have been developed recently. Besides Scanning Electron Microscopy (SEM), one of the most used equipment in cultural heritage field are further summarized: Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Direct Analysis in Real Time (DART), Surface-Enhanced Raman Scattering (SERS), Raman spectroscopy, Gas and Liquid Chromatography (GC and LC). These techniques are used for ancient textiles and also for the modern and contemporary ones.*

Key words: textile, artworks, non-destructive techniques, contemporary period, modern period.

1. INTRODUCTION

Textiles have been a fundamental part of human life since the beginning of civilization [1, 2]. Thus, like any artwork, textiles can also be divided into historical periods. Thereby, the modern components can be framed between 1860 and 1970 while the contemporary components represent any textile item from 1980 to the present.

19th centuries had the most dramatic impact on textiles. Up until that point, the production of all types of textiles - be that clothing, tapestries or just the raw materials - had been a laborious process. Everything was done by hand and, though this was time consuming, it meant that individuals had greater control over what they produced - and what they charged. The invention of automated means of production, like the power loom, posed a threat to traditional livelihoods and sparked the Luddite rebellion as workers feared they would be replaced by machines.

The purpose of this study is to summarize the methods of analysis and diagnosis of natural and synthetic polymeric materials that refer to modern and contemporary textile artworks.

One of the most important requirements for the characterization methods of textile artworks is to be non-destructive or at least micro-destructive.

2. TECHNIQUES USED IN ANALYSIS AND DIAGNOSIS OF NATURAL AND SYNTHETIC POLYMERIC MATERIALS THAT CAN BE APPLIED TO MODERN AND CONTEMPORARY TEXTILE ARTWORKS

The following methods will be discussed below: Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetry, Raman spectroscopy, Nuclear Magnetic Resonance spectroscopy, X-Ray techniques. In Table 1 are presented several techniques used in fiber identification, while in Table 2 can be found some techniques used in dyes identification.

Fourier Transform Infrared Spectroscopy is one of the most common techniques used in artworks analysis. In textile artworks and artefacts FTIR has played an important identification role for fibers, dyes and even polymers and additives used in restoration.

Differential Scanning Calorimetry (DSC) was studied as an alternative qualitative method for identifying different textile animal hair fibers. Differentiation of speciality or luxury fibers (such as cashmere) from other animal cheaper fibers (such as sheep's wool or yak) is essential to repress adulteration of textile products. Moreover, DSC analysis can be used to distinguish fibers of different types and affected by industrial textile treatments like bleaching, steaming, descaling and stretching.

Scanning Electron Microscopy (SEM) can be used to analyse the morphology of fiber and fabric surfaces. The method applied is not destructive, enabling the re-testing of the same sample with another method.

Direct Analysis in Real Time (DART) is an ion source that produces electronically or vibronically excited-state species from gases such as helium, argon, or nitrogen that ionize atmospheric molecules or dopant molecules. With the aid of DART, exact mass measurements can be done rapidly with high-resolution mass spectrometers. DART mass spectrometry has been used in pharmaceutical applications, forensic studies, quality control, and environmental studies [3].

Surface-Enhanced Raman Scattering (SERS) is a technique in which the Raman scattering signal is greatly enhanced when organic molecules with large delocalized electron systems are adsorbed on atomically rough metallic substrates; fluorescence is concomitantly quenched. SERS provides a very powerful analytical alternative for art applications.

Raman Spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. Raman spectroscopy has some unique advantages such as: non-contact and non-destructive analysis, no sample preparation needed and last, but not least, samples can be in various states such as gas, liquid, solution, solid, crystal, emulsion can be analyzed.

Liquid Chromatography is a separation technique in which the mobile phase is a liquid and the elution is, in the majority of cases, carried out in a column. Due to the fact that the an analyte properties to be analysed by liquid chromatography is its solubility in a proper solvent, there are several samples from modern and contemporary textile artworks that can be analysed by this method. There are different liquid chromatography techniques such as: High Performance Liquid Chromatography (HPLC), Ultra-High Pressure Liquid Chromatography (UHPLC), Reversed-Phase Chromatography (RP-HPLC), ion chromatography, size exclusion chromatography (SEC) and so on. Liquid chromatography techniques are used for the determination of dyes, lipids, inorganic salts (mainly anions) etc.

Gas Chromatography-Mass Spectrometry (GC-MS) is an analytical technique that can be used to identify sealants, adhesives, organic pigments and dyes [4-7].

Table 1: *Techniques used in fiber identification*

Technique	Short description of the study	Reference
FTIR	The aim of the paper was to compare various wool and hair fibers of FTIR spectra and to show the possibility of distinguishing some animal fibers and even fibers' colors. The results have shown that natural black wool spectrum can be distinguished from the white wool fiber's spectrum, while white goat hair's and black goat hair's spectra do not differ and are similar to white wool spectrum.	[8]
	In this paper was analyzed raw, alkali treated (with NaOH) and wax removed fibers of ligno-cellulosic samples and it can be observed a difference regarding the bands attributed to the stretching vibrations of C=O and C-O groups between raw and wax removed fibers compared with NaOH treated fibers. The groups mentioned before are a part of hemicelluloses and these are soluble in aqueous alkaline solutions.	[9]
	Despite their ostensible similarity, it is apparent that just minor differences in the composition of the various cellulosic plant fibers allow them to be distinguished by ATR FTIR spectroscopy, whether the fibers are presented unprocessed or in textile threads. Preliminary investigations also suggest that this technique is applicable to the characterization of such fibers in paper. There may be some ambiguity, though, when dyes or other finishing agents contribute to overlapping infrared bands, or where there is marked fiber deterioration.	[10]
DSC	Differential Scanning Calorimetry curves of different types of animal hair were compared and the fibers were identified according to the established criteria. Wool fibers show a DSC trace with a bimodal endothermic peak in the temperature range of 230–255ºC; on the contrary, cashmere DSC trace shows a single endothermic peak at 241 ºC and a shoulder at 236 ºC. The DSC curves of yak and goat fibers show a broad endothermic event at 237 ºC.	[11]
	Samples of Mohair (25.2 µm), Cashgora (20.8 µm), Cashmere (13.9 µm) and Yangir (13.6 µm) were investigated through thermal denaturation. The results revealed appreciable differences of the DSC traces in the temperature range 230-250°C.	[12]
	DSC was used for the analysis of two textiles of industrial production (used as representative modern commercial silk) and three historical silk micro-samples (weight < 2 mg; area < 1 cm^2). Considering the secondary structures of the historical samples, it was possible to hypothesize the different degradation paths followed by each sample through natural aging. By DSC analysis, the modern silk samples presented a different behavior compared to historical samples.	[13]
SEM	SEM was applied in the analysis of archaeological textile samples of finds from the Roman period and the Middle Ages. SEM analysis allowed identifying the material as flax due to "nodes" typical for linen medieval tablet-woven silk fabric. Comprehensive analysis shows that medieval wool (15th century) was much thicker than that from the 2nd century. It confirms the premise that there was a very high level of wool manufacturing in the Roman period.	[14]
	SEM was used to analyze different dyed and undyed Coptic textile samples which were collected from different Egyptian areas. After comparing all SEM photos it was noticed that the linen samples are more degraded than the wool samples. On one hand this may be due to the dyes on the wool textile, which may play a role in inhibiting the deterioration of these textiles and on the other hand it may be due to the faster deterioration of cellulosic textiles such as linen rather than than wool by the different deterioration reasons.	[15]

Table 2: *Techniques used in dyes identification*

Technique	Short description of the study	Reference
HPLC	HPLC with spectrophotometric detector has been used for the identification of compounds from textile dyes. The entire process was carried out in three stages: first, chromatographic measurements were made on purified dyes and natural dyeing substances collected from various sources. Then HPLC data were recorded for extracts of dyes from contemporary dyed fibers, which were dyed with dyestuff extracted from raw material purchased from Kremer. Finally, the extracts from fibers taken from ancient Coptic objects were analyzed under two sets of chromatographic conditions. Identification of dyes extracted from the objects was based on retention times and on UV-VIS spectra recorded for sample extracts and standards.	[16]
HPLC-PDA	In this study high liquid chromatography with diode array detectors (also known as DAD or PDA) was used in the cases of natural dyestuffs (it is well known that these natural dyestuffs contain various coloring substances). The most efficient analytical method for the determination of these dye components is the one that has at least two steps, such as: one step that leads to a separation (and thus purification) of the components (such as chromatography) and a second step: the detection of each component (spectrometry). Due to the fact that 30 and 40 years ago suitable techniques weren't yet developed it is thus advisable to recheck ancient-dye analyses.	[17]
GC-MS	This paper presents a GC–MS method with TMTFTH extraction that can be used as an alternative for dye analyses based on liquid chromatography.	[18]
	The analytical procedure based on GC-MS was applied to the analysis of standard solution of flavonoids and on non-aged and aged wool dyed specimens. The analytical procedure succeeded in identifying the flavonoid chromophores in raw materials and in dyed yarns. In fact, although a derivatization step is needed, GC-MS was proved to be a selective, sensitive and relatively fast technique.	[19]
DART	DART-MS is a sensitive, rapid and preparation-free method very useful for identifying the primary organic dye chromophores in natural fiber textiles (wool, silk, cotton and linen). Dyes were readily identified in freshly dyed textiles and in cotton skeins that were manufactured more than a century ago.	[20]
SERS	SERS analysis is maybe one of the best methods for the identification of dyes in ultramicroscopic samples of paints and glazes, at the level of specificity provided by Raman spectroscopy. SERS not only fills an important gap in the cultural heritage scientist toolbox: the application of SERS to works of art has emerged as the leading practical application of the technique.	[21]
SEM with EDAX Sapphire and Gatan CL3þ system Raman spectroscopy	The combination of more than one technique increased the reliability of the results. While Cathodoluminescence has shown a similar spectra and EDX has identified Br in the sample, only Raman spectra shows the absolute proof that the ancient and contemporary dyes are identical.	[22]
Raman spectroscopy	The characterization of the binding media and pigments in modern and contemporary paintings is important for designing safe conservation treatments, as well as for determining suitable environmental conditions for display, storage and transport. Raman spectroscopy is a suitable technique for the in situ non-destructive identification of synthetic organic pigments in the presence of the complex binding media characteristic of synthetic resin paints or color lithographic inks.	[23]

3. CONCLUSIONS

The present paper summarizes the main methods to investigate textile artworks objects. These methods are using modern equipments that show remarkable properties such as: sensibility, sensitivity, rapidity in analysis, once purchased do not show high cost of use and last, but not least, are micro or non-destructive. Moreover, these techniques can be used together for a more accurate analysis and interpretation of the samples, either archaeological or modern and contemporary.

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