Identification of changes in the surface of textiles subjected to plasma chemical treatment using attenuated total reflectance-fourier transform infrared spectroscopy

Joslyn Diana Kirkland

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Identification of Changes in the Surface of Textiles Subjected to Plasma Chemical Treatment
Using Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

by

Joslyn Diana Kirkland

Thesis
Submitted to the Department of Chemistry
Eastern Michigan University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE
In
Chemistry

Thesis Committee:
Ruth Ann Armitage, Ph.D., Chair
Krishnaswamy Rengan, Ph.D.
Ross Nord, Ph.D.

January 26, 2009
Ypsilanti, Michigan
DEDICATION

TO

MY PARENTS AND MY WONDERFUL FAMILY
ACKNOWLEDGEMENTS

I would like to thank my thesis advisor, Dr. Ruth Ann Armitage, for her patience, understanding, and guidance throughout this project. I would also like to thank my committee members, Dr. Krishnaswamy Rengan, for his support and encouragement, and Dr. Ross Nord, for his insightfulness.

I thank my research group, Reshmi Perumplavil, Jamie Brown-Sinha, Andrew Livingston, Melissa Doolin, Geneve Maxwell, Janine Van Gemert, and Mary Ellen Freund, for their help and support.

For supplying the textile samples, I thank Kathryn Jakes from Ohio State University. For the wood samples used in this project, I thank Ian Armitage of Andrews Environmental Engineering.

For financial assistance, I would like to thank the Graduate School for the graduate assistantship, the Dean’s office for a travel grant, and also the Department of Chemistry for their support.

Finally, I thank my family and friends for their support, constant encouragement, and understanding because without them none of this would have been possible.
ABSTRACT

Plasma chemical oxidation has been proposed as a “nondestructive” method for preparing samples from archaeological materials for radiocarbon dating using accelerator mass spectrometry. However, the chemical effects of low-temperature, low-pressure plasma discharges on fragile archaeological materials are not understood. It is believed that reactions only occur at the surface of the treated samples. Therefore, we have used Fourier transform infrared spectroscopy with attenuated total reflectance sampling (ATR-FTIR) to examine changes in the chemical nature of the surface of representative modern and archaeological samples upon plasma treatment. Samples that were treated with destructive wet chemical methods, e.g., treatment with sodium hydroxide solution, were compared to plasma-treated samples, as well. This work will help to clarify the efficacy of plasma treatments on archaeological materials to prepare samples for radiocarbon dating and as an alternate, less destructive, method for removing surface contamination.
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CHAPTER 1

INTRODUCTION

1.1 Introduction to Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Infrared spectroscopy is a useful technique for the qualitative and quantitative analysis of substances, generally for the purpose of identification. Most compounds with covalent bonds can absorb electromagnetic radiation. However, only bonds that have a dipole moment that changes with the molecule’s vibrational and/or rotational motion are capable of absorbing infrared radiation. The frequencies at which a molecule absorbs are consistent with its natural vibrational frequencies, which are increased in amplitude by the incoming radiation. A spectrum is constructed based on the absorption, reflection, or emission of infrared radiation, which gives molecular and structural information about a compound. With the exception of optical isomers, compounds with different structures cannot have identical infrared spectra.1,2

In 1907, Albert Michelson won the Nobel Prize for his development of the interferometer, which is the key component of a Fourier transform infrared spectrophotometer. The interferometer is a movable mirror that reflects radiation back to a beamsplitter where it is combined with reflected radiation from a stationary mirror. The recombination of the rays may result in constructive or destructive interference, depending on their phases. The new, recombinined ray passes through the sample on its way to the
detector. The difference in the pathlength from the beamsplitter to each mirror is used to calculate the retardation. A graph, called an interferogram, is constructed from the output light intensity, and the retardation is decomposed into separate wavelengths by Fourier analysis. These separate peaks are used to construct the final spectrum.\textsuperscript{3}

With the combination of Fourier transform and infrared spectroscopy in the 1970s, a higher signal-to-noise ratio, frequency resolution and reproducibility were obtained while observing the entire infrared spectrum. This method is better at studying complex mixtures and smaller quantities of sample than traditional dispersive infrared spectrometers. Since its development, FTIR has been used in the characterization of archaeological and historical artifacts for reasons including dating, authentication, determination of degradation mechanisms, and development of methods for restoration and conservation.\textsuperscript{4}

Attenuated total reflection (ATR) was developed in the early 1960s independently by Harrick\textsuperscript{5} and Fahrenfort.\textsuperscript{6} ATR is a specialized sampling technique in which samples to be studied are pressed against a highly refractive optical crystal made of such materials as zinc selenide or diamond. The infrared light is then directed into the crystal, where some of the radiation enters the surface of the sample and is absorbed. The radiation that is not absorbed by the sample is passed back through the crystal to the detector. The resulting spectrum is obtained from the ratio of total light reflected by the crystal alone and with a sample present.

The use of internally reflected beams prevents the loss of radiation with the exception of absorption by the medium. Another advantage to using ATR is that absorbance is independent of sample thickness because radiation penetrates only a few micrometers into the surface of the sample. That, along with minimal sample preparation, allows absorption spectra to be obtained nondestructively for a wide variety of sample types.\textsuperscript{1,7}
1.2 Introduction to Plasma Chemical Treatment

Plasma, the fourth state of matter, was identified in 1879 by Sir William Crookes. Occurring in nature as lightning and the Northern lights, it consists of an electrically-neutral mixture of energetic gaseous ions and atoms capable of conducting electricity. The manner in which plasma is produced in the laboratory, whether using radiofrequency (RF) energy, microwaves, or direct or alternating current, affects the temperature and reactivity of the discharge. In analytical chemistry, the high temperatures of inductively coupled RF-generated argon plasmas are exploited for emission spectroscopy and mass spectrometry. Low temperature plasmas can be generated by capacitively coupling radiofrequency (RF) energy into a low pressure gas sample. Industrial uses of argon plasmas, for example, include cleaning semiconductor surfaces\(^8\) and modification to the surfaces of implantable medical devices to improve their biocompatibility.\(^9\)

In argon plasma, the ionized argon atoms absorb the RF energy, increasing their kinetic energy. Etching occurs when the surfaces of the material exposed to the argon plasma are bombarded by these energetic ions.\(^10\) Oxygen and hydrogen, amongst other gases, can be used to produce reactive plasmas. In an oxygen discharge, the highly-reactive oxygen atoms and ions sputter and react with organic compounds from inert surfaces.

It was the selectivity of such plasmas for organic matter on surfaces that led the Rowe group at Texas A&M University in the late 1980s to use the plasma-chemical oxidation method for extracting organic carbon, in the presence of inorganic carbonates and oxalates, from archaeological samples for radiocarbon analysis. The low temperature, low pressure oxygen plasma selectively oxidized the organic carbon at the surface of the archaeological
sample to produce CO$_2$. The CO$_2$ was then radiocarbon dated by accelerator mass spectrometry.$^{11}$

1.3 Review of the Literature

1.3.1 ATR-FTIR Analysis of Archaeological Materials

In 1800, Dr. John Haslam performed a study on an “English medieval wall painting” using infrared radiation and was able to characterize six different pigments it contained.$^4$ This sparked a growing interest in the analysis of artistic and historic artifacts. With the development of modern analytical methods in the 1950s, chemists were able to apply dispersive infrared spectroscopy to this area of study. Unfortunately, dispersive instruments were slow, insensitive, and did not provide high frequency resolution, making it difficult to analyze complex mixtures.$^4$ That all changed in the 1970s with the combination of Fourier transform with infrared spectroscopy. During this period, Low and Baer explored the application of FTIR to conservation studies. They were able to conclude that this new method was better at characterizing complex mixtures and smaller quantities of sample than the traditional dispersive infrared spectrometers.$^{12}$

According to Doménech-Carbó et al.,$^{13}$ FTIR is the method of choice in the study of artifacts because it only requires a small quantity of sample. Some infrared methods, such as ATR-FTIR, can even measure whole samples without pretreatment. In one particular application, performed by Ortega-Avilés et al.,$^{14}$ only about 1 mg of sample was used to investigate the authentication of the Virgin of Sorrows painting by means of FTIR. From that small amount of sample, the varnish that was used was identified. In another example,
Doménech-Carbó and coworkers\textsuperscript{15} acquired 0.1-0.5 mg of sample from paintings and other artifacts and utilized FTIR to identify the resins in these small samples.

Paint has also been studied using the ATR sampling technique. Martin-Gil and coworkers\textsuperscript{16} used this method for the analysis of an orange-brown patina found on the surfaces of Salisbury Cathedral in hopes of identifying its composition. This quick and nondestructive technique helped to identify the components of the patina as powdered bone, an uncharacterized binder, and water, which was mixed as a plaster and applied to the walls.

Recently, Marengo et al.\textsuperscript{17} coupled infrared methods with the chemometric techniques of principal component analysis, classification methods, and cluster analysis in studies for preservation. Multivariate control charts were constructed from the analysis of painted surfaces using ATR-FTIR before and after they were subjected to artificial ageing by UV exposure. Although interpretation of the statistical analysis is difficult, there is potential that this technique could eventually be applied to real paintings for the determination of a method for conservation.

The use of ATR-FTIR to study archaeological materials is fairly widespread. Shashoua et al.\textsuperscript{18} used this technique to determine the rate of deterioration of Baltic amber samples that were aged at different levels of relative humidity. They chose ATR-FTIR specifically because it is nondestructive and has a very small sampling depth that results in measurement of just the surface where deterioration occurs. This technique is also valuable in other areas including inks, papers, and textiles.

Lang and coworkers\textsuperscript{19} used ATR-FTIR in conjunction with principle components regression (PCR) to study the gelatin content on the surface of historical papers. Their goal was to develop a method that could examine a large number of fragile materials with a
technique that was quick, nondestructive, and reproducible to estimate gelatin concentrations and other properties, such as sulfur and potassium concentrations, associated with the condition of the papers. With ATR-FTIR, they were able to accomplish this goal and were able to estimate the gelatin content as well as sulfur and potassium concentrations on the surface of the historic papers.

Studies have also been conducted on papers and how they react with ink. An example of this is the characterization of ancient manuscripts by Sistach, Ferrer, and Romero. The authors utilized ATR-FTIR to study the degradation of manuscripts as a result of microbiological agents and iron gall inks. The authors chose this technique because it does not require pretreatment of the paper and can measure an intact piece of paper or a small amount of sample, such as a fiber.

Ferrer and Sistach later conducted a study of the components of ink in ancient manuscripts. They believed that characterizing the composition of the inks could lead to an understanding of the reactions that lead to the deterioration of the paper. In the infrared spectra they obtained, the authors found peaks corresponding to oxalates, which have been previously related to some form of degradation. They concluded that there is a correlation between the pH of the ink and different cations associated with the oxalate salt. This study would not have been possible without the use of ATR due to the extremely small sample sizes that the authors were allowed to remove for analysis.

Polarized attenuated total reflectance Fourier transform infrared spectroscopy (Pol-ATR-FTIR) was made use of by Garside and coworkers in the characterization of silks to determine the proper treatment, display, and storage of historic silks. Pol-ATR-FTIR only differs from conventional ATR-FTIR in that it has a polarizer placed in the path of the
radiation before the sample. This was used to obtain 0° and 90° spectra based on the orientation of the sample fibers to the electric vector. The authors employed both ATR and Pol-ATR for the quantitative measurements of the relative β-sheet crystallinity and its orientation in artificially aged silk samples. The possible damage caused by the pressure from the ATR was assessed as well, and it was found that the applied pressure did not cause the results to stray from a reasonable range of error. Therefore, the deterioration of historic silks can be successfully studied nondestructively by use of these ATR techniques.

1.3.2 Plasma Treatment of Archaeological Materials

The paint used to make pictographs is typically thought to consist of an inorganic pigment and an organic binder. Organic carbon, without contamination by inorganic carbon, is needed to accurately radiocarbon date samples by accelerator mass spectrometry (AMS). Therefore, it was initially prohibitively destructive to radiocarbon date pictographs because of the difficulty in separating the inorganic carbon, the majority, from the organic carbon, the very small minority, needed for a diagnostic date. The Rowe group began utilizing plasma chemical treatment because it selectively removes only the organic carbon from the paint sample.\textsuperscript{11, 23}

For archaeologists, preservation of artifacts is very important. Unfortunately, the standard method for preparing samples for radiocarbon dating involves combusting a portion of the whole sample to eventually yield a graphite pellet. Removal of such a large portion of the artifact is very destructive. Steelman et al.\textsuperscript{24} first implied that plasma chemical treatment could be used as a “nondestructive” alternative to the standard method. This conclusion was
based on a study they conducted on the amount of material that was being removed from samples as a result of plasma chemical treatment. In this study, the authors visually compared samples, such as a label from a T-shirt, before and after plasma chemical treatment. Significant changes to the samples were not observed and the authors concluded that plasma chemical treatment had been shown to be “nondestructive.”

Since its development, plasma chemical extraction has been used in the direct dating of several types of artifacts. Steelman et al.\textsuperscript{25} utilized this technique to determine the date of a mummified infant bundle found in southwest Texas. Radiocarbon analysis was also performed on combusted samples for comparison of the two techniques. The results did not show a statistical difference between the dates obtained from the combusted and plasma chemical extracted samples. Based on the good precision that was obtained, the authors concluded that the infant bundle had been dated accurately.

1.3.3 ATR-FTIR Analysis of Plasma-Treated Textiles

Laguardia et al.\textsuperscript{26} used infrared spectroscopy to investigate the effects that plasma treatments had on biodeteriorated paper in hopes that plasma treatment could be used in the conservation of ancient papers. Attenuated total reflectance FTIR was used to determine if modifications were made to the surfaces of biodeteriorated paper samples as a result of plasma treatment. Spectra of treated and untreated samples did not show any significant changes, which resulted in the conclusion that plasma treatment caused minimal surface modifications to the paper. From the information that was obtained, the authors stated that plasma treatment could potentially be a new method for the restoration of ancient papers.
The identification of the molecules found in paints,\textsuperscript{4,12-17} amber,\textsuperscript{18} paper,\textsuperscript{19-20} inks,\textsuperscript{21} and textiles\textsuperscript{22} has been achieved through the application of ATR-FTIR. The characterization of some materials has provided clues to the authentication, deterioration mechanisms, and dating of artifacts. The authentication of artifacts has led to the identification of counterfeits. Dating of artifacts provides historians with information about the time period in which the artifacts were made by utilizing information such as what supplies may have been available. By determining the mechanisms for degradation, researchers have also been able to develop techniques for restoration and preservation for some works of art.

Plasma chemical extraction has been found to be a relatively “nondestructive” technique that is very useful in preparing whole fragile artifacts for radiocarbon dating by AMS. Its ability to selectively extract organic carbon has made direct dating of pictographs and other archaeological materials possible. The chemical effects of plasma chemical extraction on artifacts such as textiles have only begun to be understood.\textsuperscript{27} However, the development of this technique as a “nondestructive” cleaning method could prove to be extremely valuable to archaeologists for restoration purposes, and ATR-FTIR could be used as a nondestructive method to determine its efficacy.
1.4 Significance of the Project

The purpose of this study is to use infrared spectroscopy to qualitatively determine the chemical effects of plasma chemical treatment on archaeological materials, both simulated and authentic. The determination of plasma chemical treatment-induced chemical changes is necessary for conservation purposes.

1.5 Objectives

The objectives of this project were to:

1. Use ATR-FTIR for the qualitative analysis of plasma-treated materials.
2. Identify any chemical changes that may have occurred to the surface of sample materials as a result of plasma chemical treatment.
3. Compare changes made to materials as a result of plasma treatment to those made by different wet chemical pretreatments.
CHAPTER 2

EXPERIMENTAL

2.1 Materials

Descriptions of the materials utilized in this study are listed in Table 2.1. Textile samples were obtained through Kathryn Jakes from TestFabrics. The leather sample was purchased from a fabric store. The juniper bark, collected by Carolynne Merrell, was part of a larger artifact that was in the form of a ring. Ian Armitage unearthed the Wisconsin period wood sample in Illinois. Dr. Ruth Ann Armitage obtained the grass samples from her property. Soil humic acid standard was purchased from the International Humic Substances Society.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Chemical Composition</th>
<th>Sample Description</th>
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</thead>
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<tr>
<td>Antelope Hair</td>
<td>Protein (Keratin)</td>
<td>Modern</td>
</tr>
<tr>
<td>Charcoal</td>
<td>Cellulose (Degraded)</td>
<td>Archaeological</td>
</tr>
<tr>
<td>Cotton</td>
<td>Cellulose</td>
<td>Modern, unbleached, free of sizing and dye</td>
</tr>
<tr>
<td>Deer Hair</td>
<td>Protein (Keratin)</td>
<td>Modern</td>
</tr>
<tr>
<td>Filter Paper</td>
<td>Cellulose</td>
<td>Modern, Whatman, ashless</td>
</tr>
<tr>
<td>Grass</td>
<td>Cellulose, Lignin</td>
<td>Modern, moldy</td>
</tr>
<tr>
<td>Juniper Bark</td>
<td>Cellulose, Lignin</td>
<td>Archaeological, dirty</td>
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<tr>
<td>Leather</td>
<td>Protein (Collagen)</td>
<td>Modern</td>
</tr>
<tr>
<td>Linen</td>
<td>Cellulose</td>
<td>Modern, unbleached, free of sizing and dye</td>
</tr>
<tr>
<td>Silk</td>
<td>Protein (Keratin)</td>
<td>Modern, unbleached, free of sizing and dye</td>
</tr>
<tr>
<td>Wood</td>
<td>Cellulose, Lignin</td>
<td>Archaeological, Pleistocene, 12-15 Ka old, dirty</td>
</tr>
<tr>
<td>Wool</td>
<td>Protein (Keratin)</td>
<td>Modern, unbleached, free of sizing and dye</td>
</tr>
</tbody>
</table>
The chemical composition of natural fibers is either cellulosic (bark, charcoal, cotton, grass, paper, linen, and wood) or proteinaceous (hair, leather, silk, and wool). Most cellulosic fibers consist of a combination of cellulose, hemicellulose, lignin, and other non-cellulose materials, e.g. pectins. Cellulose, as depicted in Figure 2.1, is a linear polymer of β-D-glucopyranose units linked together by 1,4-glycosidic bonds, which give cellulosic fibers their strength. Hemicelluloses are low molecular weight polysaccharides that act as a matrix for the cellulose and a link between cellulose and lignin. Lignin is a complex, polymerized, aromatic substance with a highly-branched chain. To varying degrees, lignin is impregnated in plant cells, the amount of which is different from one plant to the next and is also dependent on the location in the plant (bark or wood). The amount of the minor constituents of cellulosic fibers is minimal.\textsuperscript{28}

![Figure 2.1 Chemical structure of cellulose](image)

Cotton, coming from seed hairs, consists of cellulose in its purest form almost completely devoid of lignin. Filter paper and linen consist almost exclusively of cellulose.\textsuperscript{28} Because lignin is photochemically oxidized by sunlight, leaving materials yellow and brittle, a chemical pulping process is used to remove lignin from most materials required to have a longer lifetime.\textsuperscript{29} Wood and bark consist of both constituents in a ratio of approximately 2:1
cellulose to lignin. Grass also contains lignin but in smaller amounts than wood.

Charcoal is a carbonaceous substance produced from organic material, e.g. wood, that has been exposed to high temperatures in the absence of air or oxygen.

Hair and wool both consist of proteinaceous fibers in which the main component is keratin. This protein contains several disulphide bonds that crosslink the cystine residues of the polymer chains, giving hair and wool their high tensile strength. Along with collagen, keratin is also found in the skin. However, it is removed during the tanning process in order to make leather. This leaves the fibrous protein collagen as the main constituent of leather products.

Silk is composed of the proteinaceous fiber fibroin. Each raw silk strand, which is produced by silkworms, is composed of two fibroin filaments that are bound together by the protein sericin. Because this protein yellows during ageing, it is removed during the degumming process, leaving single strands of fibroin, which are used in textile production.
2.2 Sample Treatment

2.2.1 Surface Contamination of Samples

Textile and leather samples, two of each, were stapled to a piece of aluminum foil-lined cardboard. The cardboard was passed around to individuals to touch the exposed surface, placing natural oils from their skin on the samples.

2.2.2 Smoke Contamination of Samples

Copal resin incense was burned, producing smoke, which was used to contaminate the surface of the textile, leather, and filter paper samples. This was done until the surfaces of the material were visibly covered in black carbon.

2.2.3 Bulk Contamination of Samples

Humic acid standard was used to pervasively contaminate the textile and leather samples. The humic acid powder was dissolved in distilled water. Aliquots of the solution were placed in separate beakers in which the samples were allowed to soak for approximately 24 hours. After being removed from the beakers, the samples were placed on clean aluminum foil in an oven and allowed to dry without heating.
2.3 Methods

2.3.1 Attenuated Total Reflectance-Fourier Transform Infrared Spectrophotometry

The primary instrumentation used for this study was a Shimadzu 8400S Fourier transform infrared spectrophotometer (Shimadzu, Columbia, MD) with a Pike Miracle single-bounce zinc selenide horizontal attenuated total reflectance (ATR) crystal (Pike Technologies, Madison, WI). The ATR had a penetration depth of 2.0 µm at 45°. The Fourier transform infrared spectrophotometer settings listed in Table 2.2 were used in each of the analyses.

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<th>Setting</th>
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<td>Resolution</td>
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</tr>
<tr>
<td>Range</td>
<td>500-4700 cm⁻¹</td>
</tr>
<tr>
<td>Beam</td>
<td>Internal</td>
</tr>
<tr>
<td>Detector</td>
<td>Standard</td>
</tr>
<tr>
<td>Mirror Speed</td>
<td>2.8 mm/sec</td>
</tr>
<tr>
<td>Mode</td>
<td>Interferogram</td>
</tr>
</tbody>
</table>
2.3.2 Plasma Chemical Treatment

Plasma was generated in a glass chamber using a 13.56 MHz radiofrequency generator. Ultra-high purity (99.999% pure) argon and oxygen gases were used to produce the plasmas, utilizing chamber pressures of 200 mtorr and 1 torr respectively. The plasma treatment conditions are listed in Table 2.3.

Table 2.3 Plasma Treatment Conditions

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>20 W(^1) Ar Plasma Treatment</th>
<th>40 W Ar Plasma Treatment</th>
<th>20 W Ar/100 W O(^2) Plasma Treatment</th>
<th>100 W O Plasma Treatment</th>
</tr>
</thead>
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<td>Uncontaminated Samples</td>
<td>30 minutes</td>
<td>30 minutes</td>
<td>30 minutes/10 minutes</td>
<td>60 minutes</td>
</tr>
<tr>
<td>Cotton, Leather, Linen, Silk, Wool</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>30 minutes</td>
<td>N/A</td>
<td>60 minutes</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>30 minutes</td>
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<td>60 minutes</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Touch-Contaminated Samples</td>
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<td>30 minutes/10 minutes</td>
<td>60 minutes</td>
</tr>
<tr>
<td>Cotton, Leather, Linen, Silk, Wool</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naturally-Contaminated Samples</td>
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<td>N/A</td>
<td>60 minutes</td>
</tr>
<tr>
<td>Grass and Wood</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antelope Hair, Deer Hair, Charcoal, Juniper Bark</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>60 minutes</td>
</tr>
</tbody>
</table>

\(^1\) Watts  
\(^2\) Argon/Oxygen
2.3.3 Wet Chemical Pretreatment

Wet chemical pretreatments were performed on the textile, leather, grass, and wood samples using sodium hydroxide (the standard method) and pH 8 phosphate buffer (a newly proposed treatment method) solutions both at a 1 M concentration. Small amounts of each sample were placed in individual microcentrifuge tubes to which 1 mL of solution was added. The tubes were inverted to ensure mixing before being placed into a sonicating water bath (50 ± 5°C) for 60 minutes. Upon removal from the water bath, the tubes were centrifuged briefly and the solution was removed. This procedure was repeated until the resulting solution was clear, indicating that the sample was considered clean.
3.1 The Effect of Argon and Oxygen Plasma

3.1.1 The Effect of Argon and Oxygen Plasma on Uncontaminated Samples

The first step to understanding the chemical effects of plasma treatment on archaeological samples was to subject uncontaminated samples to various plasma treatments and compare the infrared spectra obtained to that of the samples prior to treatment. Argon plasma treatment has been used as a technique for removing or “sputtering” surface contamination before an archaeological sample was subjected to an oxygen plasma to extract organic carbon for radiocarbon dating. Comparison of the infrared spectra of the argon plasma-treated textile and leather samples to their original infrared spectra did not show any significant changes with the exception of cotton. In Figure 3.1, an increase in the peak representing the C=O stretching of an ester can be observed. This peak can represent the carboxylic acid found in pectin. However, it is not found in the spectrum for the unaltered sample; therefore, it most likely represents the carboxylic acid of oxycelluloses found in degraded samples. Denes et al. reported the identification of a carbonyl peak that was believed to be a result of the oxidation of the free radicals formed by the cleavage of the C1-C2 bonds of the pyranosidic ring of cellulose induced by argon plasma treatment.
During treatment with oxygen plasma, discoloration of the leather, silk, and wool samples was observed. Some discoloration of the cotton and linen samples was observed as well, but to a lesser extent. Comparison of the infrared spectra obtained did not indicate that any changes were being made chemically to the surface of the samples as a result of this process with the exception of cotton. Similar to the spectrum for the argon plasma-treated cotton sample (Figure 3.1), the oxygen plasma-treated sample has a peak around 1730 cm$^{-1}$. According to Denes et al.\textsuperscript{36} and Malek et al.\textsuperscript{37} this peak appears as the result of the action of oxygen on the free radicals formed by plasma treatment on the cellulose fibers. Figure 3.2 illustrates an example of the lack of changes made to the rest of the samples as a result of oxygen plasma treatment. The changes that were observed can be related to desiccation as a
result of the vacuum environment of the chamber. The photos in Figure 3.3, for example, show the difference in appearance of the leather sample before and after oxygen plasma treatment along with a comparison of its infrared spectra.

Figure 3.2 Infrared spectra of an unaltered (top) and oxygen plasma-treated (bottom, bold) silk sample
In order to further understand the effects of plasma treatment on archaeological artifacts, textile and leather samples were subjected to an argon plasma treatment immediately followed by an oxygen plasma treatment. This follows the method that is currently used to extract samples for radiocarbon dating. Of the samples that were treated, cotton, wool, and leather exhibited changes in their infrared spectra. As observed before, the peak at 1730 cm\(^{-1}\) appeared in the spectrum for the treated cotton.

The change observed in the spectrum for wool, illustrated in Figure 3.4, was not as obvious and only appeared in the spectrum obtained from the edge of the sample on the side that was exposed to the plasma. Ryu et al.\(^{38}\) reported that C=O and COOH functional groups

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**Figure 3.3** Photos and infrared spectra of an unaltered (bottom) and oxygen plasma-treated (top, bold) leather sample
are added to the fiber surface of wool samples as a result of low-temperature oxygen plasma treatment. Studies performed by Sweetman\(^{39}\) indicate that this is the result of the degradation of keratin caused by the temperature of the plasma chamber being above 100°C. Although silk is similar in composition to wool in that they are both composed of proteins, studies by Walde et al.\(^{40}\) indicated that wool is more easily degraded than silk at high temperatures.

Figure 3.4 Infrared spectra of unaltered (bottom) and argon/oxygen plasma-treated (top, bold) wool
The spectra for leather prior to any plasma treatment, after argon plasma treatment, and after oxygen plasma treatment all included a peak at 1740 cm\(^{-1}\), which is attributed to the C=O of carboxylic acid. After the sample of leather was subjected to the combination of argon and oxygen plasma treatments, this peak no longer appeared in the spectrum, as illustrated in Figure 3.5. The removal of this peak is most likely the result of oxidative decarboxylation, a deterioration mechanism of the amino acids found in collagen.\(^{41}\)

![Infrared spectra of an unaltered (bottom) and argon/oxygen plasma-treated (top) leather sample](image)

**Figure 3.5 Infrared spectra of an unaltered (bottom) and argon/oxygen plasma-treated (top) leather sample**
3.1.2 Effect of Argon and Oxygen Plasma on Naturally Contaminated Samples

Samples, both archaeological and modern, were collected to study the effects of plasma treatment on naturally contaminated materials. Modern antelope hair and deer hair along with archaeological juniper bark and charcoal were subjected to oxygen plasma treatment. During treatment, the antelope and deer hair turned from white to almost transparent and became very brittle. As illustrated in Figures 3.6 and 3.7, the hair samples underwent further oxidation of the carboxylated groups resulting in the loss of carbon from the fatty acid chains in the form of CO\textsubscript{2}, which was evident by the decrease in the peak representing C=O stretching.\textsuperscript{42}

![Figure 3.6 Infrared spectra of unaltered and oxygen plasma-treated (bold) antelope hair](image)

Figure 3.6 Infrared spectra of unaltered and oxygen plasma-treated (bold) antelope hair
Oxidation of cystine monoxide to form cystine dioxide groups also occurred as a result of the oxygen plasma treatment. This can be attributed to the oxidation of the disulfide bond in cystine.\textsuperscript{43} This same observation was made by Molina et al.\textsuperscript{42} who used XPS to characterize the surface of plasma treated keratin samples. Because disulfide bonds are important in holding together the proteins found in hair and giving it some rigidity, oxidation of these bonds causes the structure of hair to weaken and become brittle. This change in structure further explains the physical changes that were observed visually in the hair samples.
Although the spectra obtained from the charcoal sample did not illustrate any significant changes as a result of the oxygen plasma treatment, Figure 3.8 illustrates the changes made to the juniper bark sample. Significant changes in peak intensity were observed, but the most interesting changes occurred to the O-H peak, asymmetric and symmetric C-H stretching peaks, and C-O guaiacyl ring peak. These changes are most likely a result of the outer surface layer containing contaminants being removed. This allowed a new layer to be exposed and studied, which consisted of the cellulose and lignin of the bark instead of the contamination. Therefore, shifts and significant changes were observed when the unaltered and oxygen plasma-treated spectra were compared.

Figure 3.8 Infrared spectra of unaltered (top) and oxygen plasma-treated (bottom, bold) juniper bark
Like the other modern samples, a naturally contaminated grass sample was also subjected to oxygen plasma treatment. The changes that were made chemically to the surface of the sample were obvious in a comparison of the infrared spectra. The C-H and C=O stretch bands that were present in the spectrum for the unaltered sample had decreased significantly as a result of oxidation. This was apparent by the dry and brittle appearance of the grass sample after plasma treatment, which is attributed to the decomposition of cellulose. The more important changes, though, were observed between 1300 and 500 cm$^{-1}$ as depicted in Figure 3.9. The significant differences in this area of the spectra are probably the result of the removal of mold contamination, most likely *Aspergillus* sp. It was observed that the side of the grass sample that was exposed to the plasma appeared “cleaner” than the unexposed side. It is believed that the changes in the infrared spectra can be attributed to the removal of the mold contamination and exposure of the cellulose and lignin composition of the grass sample.
Mold-contaminated grass samples were subjected to 20 W and 40 W argon plasma treatments to determine if contamination could still be removed with a plasma treatment at a lower radiofrequency power. Comparison of the two spectra that were obtained for the sample that was exposed to the 20 W argon plasma did not show any variations. The only difference between these spectra and the unaltered spectrum was a significant decrease in the C-H and C=O stretch peaks as a result of oxidation. These observations are consistent with those reported by Laguardia et al.\textsuperscript{26} who used ATR-FTIR to confirm the removal of carbonaceous contamination of an aliphatic nature\textsuperscript{45} by studying the decrease in C-H and O-H peaks in the spectra for contaminated, argon plasma-treated paper.
A comparison of the spectra obtained from the exposed and unexposed surfaces of the grass sample treated with a 40 W argon plasma did show considerable differences. As revealed in Figure 3.10, the area between 1250 and 500 cm\(^{-1}\) contains several peaks that are different between the two spectra. When the spectrum for the unaltered sample is added into the comparison, as depicted in Figure 3.11, it can be seen that this spectrum is similar to the spectrum for the unexposed surface of the treated sample. Therefore, it is believed that the mold contamination was removed from the side of the grass sample that was directly exposed to the plasma, resulting in an infrared spectrum of cellulose and lignin instead of the mold covering the surface of the grass.

Figure 3.10 Infrared spectra of the exposed surface (#1, top) and unexposed surface (#2, bottom, bold) of a 40 W argon plasma-treated moldy grass samples
Figure 3.11 Infrared spectra of an unaltered (bottom) grass sample and the exposed (#1, top, bold) and unexposed (#2, middle) surfaces of a 40 W argon plasma-treated grass samples

The unaltered moldy grass sample and grass samples exposed to the 20 W and 40 W argon plasmas were compared. Similarities were found between the unaltered, 20 W argon plasma-treated spectrum and the unexposed surface of the 40 W argon plasma-treated spectrum in that they did not show any significant alterations. The spectrum for the exposed surface of the 40 W argon plasma-treated sample was, again, significantly different from the rest of the spectra. Based on this comparison, it is believed that not all of the mold contamination on the surface of the grass was removed by a 20 W argon plasma treatment. Once the contamination was completely removed by a 40 W argon plasma treatment,
significant differences in the infrared spectrum were observed for the side of the grass sample that was directly exposed to the plasma.

An ancient (~12-15,000 years old) wood sample found buried in the ground was subjected to an oxygen plasma treatment. Spectra were obtained from both sides of the sample for comparison. The fingerprint regions of the spectra obtained from the exposed and unexposed surfaces of this wood sample were found to be very different. As illustrated in Figure 3.12, the spectrum for the unaltered sample was similar to the spectrum of the unexposed surface of the treated wood sample. With one side of the sample appearing visually “cleaner” than the other, it is believed that the contamination was removed from the surface of the sample resulting in an infrared spectrum of the cellulose and lignin composition of the wood instead of the “dirt” contamination.
Like the mold-contaminated grass sample, argon plasma treatments at 20 and 40 W were carried out on “dirty” wood samples. The spectra for both of the argon plasma-treated samples were similar to the spectrum for the unaltered wood with the exception of changes in intensity of the peaks at 1400 and 864 cm\(^{-1}\) (Figure 3.13). Based on the comparison of the 20 and 40 W argon plasma treatment spectra, it must be concluded that the “dirt” contamination was not removed from the surface of the wood sample by either of the argon plasma treatments. Taking into consideration the pervasiveness of the contamination and the depth at which it is believed the argon plasma is capable of etching into the surface of
a sample, it was expected that not all of the contamination would be removed from the wood sample, leaving little to no change in the infrared spectrum.

Figure 3.13 Infrared spectra of an unaltered wood sample (top) and 20 (bottom) and 40 W (middle, bold) argon plasma-treated wood samples
3.2 Plasma Treatment as a Cleaning Method

3.2.1 Plasma treatment of smoke-contaminated samples

Smoke is a common surface contaminant found on archaeological samples. Possible causes of smoke contamination include cooking over an open flame or burning candles and incense during religious ceremonies. Because argon atoms are relatively large and inert, it was thought that argon plasma treatment could be used to gently remove the soot from the surface of the textile samples. Therefore, smoke-contaminated textile, leather, and filter paper samples were subjected to 20 and 40 W argon plasma treatments. The spectra acquired from the treatments at these two radiofrequency powers were compared, but significant variations were not found for any of the samples. As demonstrated in Figure 3.14, spectra produced for samples subjected to these two radiofrequency powers resulted in almost perfect overlays upon comparison.
When the unaltered spectra were compared to the spectra of the 20 and 40 W argon plasma-treated samples, however, some variations were found between the pre- and post-plasma treatment results. The most obvious change was the dramatic shift in the baseline from the pre-plasma treatment spectra to the post-plasma treatment spectra. The other change observed was the presence and disappearance of peaks around 2100 and 1996 cm$^{-1}$ from pre- to post-plasma treatment as depicted in Figure 3.15. These peaks can most likely be attributed to the presence of carbon monoxide found in the soot contamination that formed on the surfaces of the textile and leather samples.$^{46,47}$ It is interesting to note that these peaks
are not only present in the spectra for the smoke-contaminated samples but in those for charcoal, as well.

The smoke-contaminated textile, leather, and filter paper samples were also subjected to an oxygen plasma treatment. As illustrated in Figure 3.16, the same two peaks around 2100 and 1990 cm\(^{-1}\) were observed disappearing as a result of the oxygen plasma treatment. The only other variations that were observed upon comparison of the spectra were decreases in intensity of some peaks and shifts in the baseline.
Figure 3.16 Infrared spectra of unaltered (bottom) and oxygen plasma-treated (top, bold) smoke-contaminated leather samples

Filter paper was the only exception to these observations. Like the spectra for the other smoke-contaminated samples, peaks around 2100 and 1990 cm\(^{-1}\) were observed in the pre-plasma spectrum for filter paper. These same two peaks were also observed disappearing in the spectrum for the oxygen plasma-treated sample. The difference between the filter paper and the rest of the samples was that a decrease in peak intensity did not occur from pre- to post-plasma spectra. Instead, the peak intensities increased, most likely as a result of the surface contamination having been removed during the plasma treatment (Figure 3.17). The more intense peaks that appeared in the post-plasma spectrum represent the cellulose fibers of the paper sample.
Figure 3.17 Infrared spectra of unaltered (bottom) and oxygen plasma-treated (top, bold) filter paper

Although significant chemical changes were not observed in the infrared spectra of the smoke-contaminated samples, physical changes were observed visually. All of the samples appeared cleaner as a result of the 20 and 40 W argon plasma treatments (Figure 3.18). However, the textile samples also seemed to have yellowed in the process. The yellow appearance of the cellulose textiles can be attributed to photooxidation and dehydration, causing the formation of conjugated ethylenic carbonyl groups that reflect the color yellow. The oxidation of tyrosine and tryptophan along with the accompanying formation of carbonyl groups from waxes and lipids present in residual, naturally-found grease is responsible for the yellowing of wool textiles. Silk textiles yellow as a result of the
oxidation of tryptophan.\textsuperscript{48} The leather sample was the only sample that did not yellow. It did appear darker in color, though, which was most likely a result of shrinking due to the desiccating environment of the low pressure chamber.

The oxygen plasma treatment was also successful in removing some of the surface contamination from the samples, which is consistent with the findings of Rutledge et al.\textsuperscript{49} who used plasma treatment to remove smoke contamination from paintings. As depicted in Figure 3.19, the oxygen plasma treatment appears to have removed more of the contamination from the cotton sample than either of the argon plasma treatments. The oxygen plasma treatment did not result in yellowing of the textile samples unlike the argon plasma treatments. Unfortunately, silk and wool were completely charred while they were under the low pressure of the chamber overnight before the plasma treatment was performed (Figures 3.20). Because this had not occurred previously in any other experiment, it is not clear as to why this happened.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{unaltered_20W_Ar_40W_Ar_Oxygen_treatment}
\caption{Photos of unaltered, 20 and 40W argon plasma-treated, and oxygen plasma-treated filter paper samples}
\end{figure}
3.2.2 Plasma Treatment of Sebum-Contaminated Samples

A considerable amount of contamination found on archaeological samples can be attributed to the modern-day handling of artifacts by people with their bare hands. Sebum, the naturally occurring oil found on the skin, is transferred to the surface of an artifact during handling, leaving behind a residue. Given that $^{14}$C has a half-life of 5730 years, there is a greater abundance of $^{14}$C in a modern residue than in the artifact itself. The addition of $^{14}$C...
from the contamination results in a higher ratio of $^{14}$C to $^{12}$C. Therefore, the age of the contamination will make the artifact appear much younger than it actually is if the modern contamination is not removed prior to radiocarbon dating.

While sebum is composed of waxes and squalene, over half of its composition consists of free fatty acids and triglycerides. This is evident by the peak around 1740 cm$^{-1}$ in the infrared spectrum identified as the carbonyl of the ester linkages of lipids. This peak is most likely due to the presence of the triglyceride tricaprin. As illustrated in Figure 3.21, a comparison of the contaminated and uncontaminated fabric samples confirms the addition of sebum on the linen, silk, and cotton samples. The presence of this peak in the spectrum for the contaminated wool was less significant. The spectrum for leather already contained a peak at this wavenumber, making it impossible to observe the presence of a peak resulting from the addition of sebum.
Observing peaks at 2920 and 2850 cm\(^{-1}\) (asymmetric and symmetric methylene stretch) is also an indication of the presence of free fatty acids and triglycerides. Although peaks are generally found in this area due to the composition of the fabric samples, those appearing as a result of the sebum should be located at slightly different wavenumbers than those of cellulose and keratin. In Figure 3.22, a peak at 2916 cm\(^{-1}\) appeared in the spectrum for the contaminated cotton sample alongside the methylene stretch peak. Even though the presence of these peaks alone does not indicate contamination by sebum, they can be used together to confirm its presence.
As before, it was believed that an argon plasma treatment could be used prior to an oxygen plasma treatment to remove surface contamination. Comparison of the spectra obtained before and after the treatment showed definite differences for the cotton, linen, and silk fabrics. Any changes in the surface of the leather sample were not observed due to the presence of peaks already in the specified areas. For cotton and linen, the carbonyl stretch band at 1735 cm\(^{-1}\), previously identified as the carbonyl of the ester linkage of a lipid, was replaced by a peak at 1716 cm\(^{-1}\) representing the carbonyl stretch for free fatty acids instead (Figure 3.23). The carbonyl band was no longer present in the post-treatment spectrum for the silk sample, which indicates that the sebum contamination was removed.
definition in the spectrum of wool made it difficult to determine if a deletion of the carbonyl band occurred. However, deletion of the methylene peak at 2850 cm$^{-1}$ does help to indicate that sebum was removed from the surface of the wool sample.

Figure 3.23 Infrared spectra of unaltered (bottom) and argon plasma-treated sebum-contaminated (top, bold) linen samples

Fabric and leather samples were also subjected to an oxygen plasma treatment as well as an argon plasma treatment immediately followed by an oxygen plasma treatment (argon/oxygen plasma treatment). Any differences in the spectra for the leather sample that may have resulted from these plasma treatments were not observed due to the presence of peaks already in the areas of interest. The spectra for the oxygen plasma-treated and
argon/oxygen plasma-treated cotton, linen, silk, and wool samples were similar in that none of them had distinct peaks at 2920 and 2850 cm\(^{-1}\) (Figure 3.24). The spectra for the plasma-treated cotton and linen were similar in that the carbonyl peak at 1740 cm\(^{-1}\) did not appear for either fabric. As illustrated in Figure 3.25, the peak for the carbonyl of free fatty acids at 1720 cm\(^{-1}\) appeared in the spectra for both cotton and linen as a result of oxygen plasma treatment and argon/oxygen plasma treatment. The spectra for argon plasma-treated and argon/oxygen plasma-treated silk showed the absence of a peak at 1740 cm\(^{-1}\) without the addition of a peak at 1715 cm\(^{-1}\). Because the carbonyl band did not appear in the spectrum for wool prior to plasma treatment of the sample, it was not expected nor did it appear in the oxygen and argon/oxygen treatment spectra.

![Infrared spectra of unaltered (bottom), oxygen plasma-treated (middle), and argon/oxygen plasma-treated sebum-contaminated (top, bold) silk samples](image)

Figure 3.24 Infrared spectra of unaltered (bottom), oxygen plasma-treated (middle), and argon/oxygen plasma-treated sebum-contaminated (top, bold) silk samples
3.2.3 Plasma Treatment of Humic Acid-Contaminated Samples

Humus, the organic material found in soil, is composed of humic substances. Humic acid is one of the major components of the humic substances. When an artifact is buried, it becomes contaminated by humic acids. Because water naturally percolates through most soils, humic acid contamination is much more pervasive than smoke and sebum contamination, which should be limited to the outer exposed surfaces. Because plasma only interacts with the surface of a sample, removal of pervasive contamination is much more difficult. If the contamination is not removed prior to radiocarbon dating, however, it can yield a much less accurate date than that of the actual age of the sample.
The infrared spectra of the humic acid-contaminated textile and leather samples were obtained and compared to the infrared spectra of the samples prior to contamination. This was performed to locate peaks that could be attributed to the contamination. Hay et al.\textsuperscript{53} identified two peaks at 1720 and 1590 cm\textsuperscript{-1} as the C=O stretch of a carboxyl group and the asymmetric stretch of a carboxylate group, respectively, in their study of natural organic materials that included humic acid. Unfortunately, these peaks were identified in the infrared spectra for the cotton and linen samples only after plasma treatment. The peak at 1720 cm\textsuperscript{-1} also appeared in the uncontaminated, plasma-treated cotton and linen samples, as was discussed previously. The peak at 1590 cm\textsuperscript{-1} was not previously identified and can be attributed to the humic acid contamination. By removing the H-O-H bend peak, the asymmetric stretch peak of the carboxylate group indicating humic acid contamination was revealed. These bands were not identified in the leather, silk, and wool samples, most likely because they were located in the same area as the amide I band.

The contaminated textile and leather samples were subjected to argon plasma treatment in hopes of removing the humic acid contamination. The leather, silk, and wool samples did not present any changes in their spectra as a result of the treatment. The cotton and linen samples did exhibit a change in their infrared spectrum, which can be attributed to the desiccation of the fabrics, as previously discussed. Figure 3.26 illustrates this change in the spectra for cotton. All of the samples appeared visibly “cleaner” as a result of the argon plasma treatment.
Humic acid-contaminated textile and leather samples were also treated with an oxygen plasma. Comparison of the spectra obtained before and after treatment indicated that changes did not occur to the leather, silk, and wool samples. This is interesting considering the silk and wool samples appeared to have charred during the plasma treatment process. As with the argon plasma-treated samples, the changes that occurred to the cotton and linen samples were attributed to the desiccation of the fabrics. Figure 3.27 illustrates the changes made in the spectra of the oxygen plasma-treated linen sample. Overall, the cotton, linen, and leather samples appeared visibly “cleaner” as a result of the oxygen plasma treatment. However, with both the argon plasma-treated and oxygen plasma-treated cotton and linen...
samples, the peak representing the humic acid contamination was present after treatment, indicating that not all of the contamination was removed.

Figure 3.27 Infrared spectra of unaltered (bottom) and oxygen plasma-treated humic acid-contaminated (top, bold) linen samples
3.3 Comparison of Plasma Treatment to a Standard Pretreatment Method

Humic acid and naturally-contaminated samples were subjected to a wet chemical pretreatment method. This is the standard process for removing contamination from archaeological artifacts prior to subjecting them to plasma chemical oxidation to collect samples for radiocarbon dating. Sodium hydroxide, the base commonly chosen for this method, is very destructive to archaeological samples in that it hydrolyzes the carbohydrate linkages in cellulose and peptide bonds in protein structures. The fabric and leather samples were pretreated using sodium hydroxide (1 M) to compare the effects of this method to those of argon and oxygen plasma treatment.

Of the samples that were treated with sodium hydroxide, leather, silk, wool, and wood were affected the most. The sodium hydroxide solution disintegrated these samples to the point of liquefying them. The infrared spectra for cotton and linen did not show any significant changes chemically. As depicted in Figure 3.28, these samples did appear visually “cleaner” after the sodium hydroxide treatment. However, their weaves did appear looser and frayed around the edges, which would be damaging to an archaeological artifact.

![Figure 3.28 Photos of humic acid contaminated cotton and linen samples before and after treatment with sodium hydroxide solution](image-url)
The moldy grass sample was the one sample that showed significant differences in the infrared spectrum as a result of the sodium hydroxide pretreatment. As illustrated in Figure 3.29, the peaks at 2920, 2850, 1730, and 1244 cm\(^{-1}\) have decreased considerably. This could be attributed to the removal of the mold contamination by the sodium hydroxide solution. That would result in a spectrum of the cellulose and lignin instead of the mold contamination on its surface of the grass sample.

![Figure 3.29 Photos and infrared spectra of unaltered (bottom) and sodium hydroxide pretreated mold-contaminated (top, bold) grass samples](image)

**Figure 3.29** Photos and infrared spectra of unaltered (bottom) and sodium hydroxide pretreated mold-contaminated (top, bold) grass samples
The textile, leather, grass, and wood samples were subjected to the wet chemical pretreatment method using a pH 8 phosphate buffer (1M). It was believed that a less harsh buffer solution could be used to successfully remove contamination in place of the traditionally used sodium hydroxide solution, which is damaging to an artifact. Of the samples that were treated, cotton, grass, linen, silk, wood, and wool did not show any significant changes in their infrared spectrum after treatment. They did appear visibly “cleaner,” and the weave of the textiles appeared to be intact. However, contamination could still be seen on the surfaces of these samples.

Although they did not appear visibly altered, the infrared spectra for the phosphate buffer-treated leather samples did show some slight variations. As shown in Figure 3.30, two peaks at 1060 and 985 cm$^{-1}$ appeared in the spectra for both the humic acid-contaminated and uncontaminated leather samples that had undergone pretreatment. These two peaks were not observed in the spectra for the uncontaminated or humic acid-contaminated samples that did not undergo pretreatment. These peaks could be the result of phosphate esters forming on the surface of the treated leather samples.
Figure 3.30 Infrared spectra of an uncontaminated, untreated leather sample (middle) and contaminated (top, bold) and uncontaminated phosphate buffer-treated (bottom) leather samples.
CHAPTER 4

CONCLUSIONS

4.1 General Conclusions

Discoloration of the modern, representative textile and leather samples occurred as a result of the argon and oxygen plasma treatments. The samples appeared dry due to the desiccation that occurred as a result of the vacuum environment inside the chamber. The textile samples were found to yellow upon exposure to ultraviolet light originating from the plasma being produced.

Chemical changes were found to have occurred in the textile and leather samples that were used in this study. Comparisons of the infrared spectra of the samples from before and after plasma treatment supported the conclusions that photooxidation had occurred. The peaks representing the formation of oxycellulose in cotton and linen samples and the degradation of keratin in silk and wool samples were found in the infrared spectra of the samples after plasma treatment, explaining the yellow discoloration.

Surface contamination from smoke, mold, sebum, and soil was removed from the samples in varying degrees dependent on the material and extent of the exposure to the contamination. Contamination on the outermost surface of a sample, such as mold and sebum, was removed effectively by plasma treatment. Smoke and soil contamination, which penetrated further into the surface of the samples, was not as easily removed.

Plasma treatment is effective as a cleaning tool for the removal of surface contamination from samples, but not as effective for the removal of pervasive contamination.
such as that from humic acid. Although the materials appeared “cleaner,” the complete removal of contamination from the samples did not occur as a result of plasma treatment. This was confirmed by the presence of peaks resulting from humic acid contamination observed in the infrared spectra of the plasma-treated samples compared with that of the unaltered samples. Because the failure to remove all contamination causes an inaccurate radiocarbon date to be calculated, it is imperative that a pretreatment method be used to remove any contamination from an artifact prior to being radiocarbon dated.

In general, materials that have undergone plasma treatment are visually preserved with minimal chemical changes occurring to their surfaces. The success of argon and oxygen plasma treatment in removing contamination from the surface of materials to be radiocarbon dated varies. Humic acids and other forms of pervasive contamination may not be completely removed by plasma treatment. Therefore, the removal of contamination is strongly dependent on how far the plasma penetrates into the material to be dated.

4.2 Future Analyses

To further study the chemical effects of plasma treatment to the surface of materials, it will be necessary to use x-ray photoelectron spectroscopy (XPS). This method is more sensitive and spatially selective and will provide a quantitative analysis of any chemical changes that occur to the outermost surface of a sample. Other ATR crystals such as silicon/zinc selenide (Si/ZnSe) or diamond, which are more sensitive and allow the infrared radiation to penetrate less into the surface of the sample, may help to identify any chemical changes made to plasma-treated materials.
Future studies using plasma chemical oxidation may also take place in conjunction with the British Museum. The focus of that study would be on using plasma chemical oxidation to remove contamination from waterlogged, dyed textiles. This would allow for further analysis of the dyes.
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