Short communication

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Depth profiling laminated glass with a fiber optic probe customized for adjustable working distance†

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Fiber optic probes allow for *in situ* characterization of cultural heritage objects and analysis of materials that are difficult to access. Positioning these probes is challenging in terms of focal distance, angle of analysis, and stability. Modifications to improve control include stabilizing the probe against a stationary surface, typically mediated by a tripod, or against the artifact itself with a distance regulating sheath that fixes the focal point at the object surface. The first makes the system less portable, while the second eliminates depth profiling capability. An adjustable working distance adapter was created that allows the operator to position a fiber optic probe against the surface of a transparent artifact and move the working distance up to 6 mm into the material while excluding ambient light. The hollow adapter contains no optical fiber, lenses, or windows, so optics are dictated by the fiber optic probe. The tool was created to study the polymeric interlayers in laminated safety glass used in early 20th century aviation and also could be applied to contemporary laminated glass, other multilayer transparent objects, and substances in transparent containers. Published 2014. This article is a U.S. Government work and is in the public domain in the USA.

Keywords: portable Raman; adjustable working distance; laminated glass; fiber optic; cellulose nitrate

Introduction

Fiber optic probes are valuable tools for *in situ* analysis of cultural heritage objects. They allow for analysis of materials that are not easily accessible because of their location, orientation, fragility, or sampling restrictions.[1] Positioning these probes is challenging in terms of focus, angle of analysis, and stability.[2–4] The benefits of a lightweight probe quickly are negated by a shaky human hand. This is particularly true for longer analyses that often are required when the Raman signal is weak or noisy, due to either the nature of the sample or the operator's desire to reduce risk of damage to the artifact by limiting the excitation laser power.

Control can be improved by stabilizing the probe against a stationary surface, typically mediated by a tripod or other stand, or against the artifact itself with a sheath that fits over the end of the fiber optic probe and fixes the focal point at the object surface.[2–5] Tripod type solutions now are used routinely for analysis of vertical surfaces including paintings and architectural elements and can be equipped with adjustable fine positioning stages for focusing. However, tripods and other stands have limitations. First, the angle of analysis usually is restricted and may not suit the orientation of the artifact. Bulky stands are cumbersome, can create tripping hazards, and are liable to tip into artifacts; this is particularly worrisome in awkward gallery spaces. Furthermore, interference from ambient light can prevent collection of usable spectra, but working in the dark (i.e., outdoors or in a public space) often is not possible. When darkness is an option, risk to the artifact is increased because the operators cannot see what they are doing. Excluding ambient light by covering the analytical set up with draped fabrics or aluminum foil is clumsy and tiring for the team, which also increases risk to artifacts.[4]

Another option is a detachable distance regulating tube that fits over the fiber optic probe and is placed directly against the artifact surface.[2,5] Part of the allure of Raman spectroscopy is non-contact analysis, which can be important for fragile artifact surfaces. However, with cultural heritage the overarching goal is to avoid damage (or undue risk to) the artifact. Working together, a conservator and scientist may decide that stabilizing the instrument against the artifact is a valid option. There are artifacts that will not be disturbed by direct, gentle contact with the probe head, and this is true of the chemically stable window glass described in this communication. A fiber optic probe sheathed with a distance regulating tube is lightweight, which can be safer for fragile artifacts than a handheld spectrometer, the typical weight of which can range from 0.5–6 lbs (0.3–2.7 kg). It is easy to position perpendicular to any exposed surface, and the tube excludes ambient light. The drawback is that the ability to adjust the depth of analysis is lost.

As part of a study of laminated safety glass used in early aviation, the authors designed a tube adapter that fits over the fiber optic probe head and allows the operator to adjust the working

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distance while stabilizing the probe against the artifact surface and eliminating ambient light. This allowed for analysis of polymeric interlayers in historic laminated safety glass.

Adjustable focal length adapter

The adapter is constructed of two machined aluminum tubes that are threaded one over the other (Fig. 1a and b). The adapter's inner tube fits over the fiber optic probe shaft. Its inside diameter is matched to outside diameter of the probe shaft, and they have the same length. A rubber O-ring in a concentric groove on the tube interior provides a friction fit. The second aluminum tube is shorter, and its inside diameter is matched to the outside diameter of the first tube, over which it is threaded. The far end of the second tube is finished flat and is the contact point for the artifact. The adapter is hollow, without optical fiber, lenses, or windows, so the focusing parameters and confocality are dictated by the fiber optic probe and the spectrometer.

To collect a spectrum, the adapted probe is placed against the material that will be analyzed, and the depth of the focal point is adjusted by winding the outer tube back or forth. Maximum focal depth is achieved when the ends of the two tubes are even and is limited to the focal distance of the fiber optic probe (Fig. 1b and c). Winding the outer tube forward moves the focal point back out toward the surface of the material.

For our prototype, working distance is continuously adjustable in micron scale increments, where one full revolution changes the focal length by 1.19 mm (3/64 in.). The entire focal range of our fiber optic probe (5.9 mm, ~1/4 in.) is spanned in 4.96 revolutions. The travel was chosen empirically but could be calculated precisely to suit the lens of any focused fiber optic probe and desired analytical depth.

Case study: laminated safety glass

The idea for an adjustable working distance adapter was conceived during a technical study of polymers used in early aviation by the Smithsonian's Museum Conservation Institute and National Air and Space Museum. A portable B&W Tek MiniRam II dispersive Raman spectrometer with a fiber optic probe (Model #BAC100-785) was used to analyze nine aviator goggles with lenses of laminated safety glass, where the polymer of interest is encased between two sheets of glass and could not be accessed directly. This was a new approach to studying laminated glass. Previous published studies, outside the cultural heritage field, characterize the polymer or the polymer-glass interface using experimentally prepared, open face mock-ups or after deconstructing the laminate.[6–8] Neither is appropriate for studying intact historic artifacts. Any characterization of the polymer interlayer would have to be performed through the glass, so Raman spectroscopy was a valuable tool.

Goggles that survive from the World War I period are fragile and do not lie in an orientation that suits typical analytical setups that use a tripod or stand. Other historic aviation artifacts studied, such as airplane windshields, also are challenging to access with a spectrometer because of their height above the ground and recessed position relative to the airplane's edge. A fiber optic probe modified with the adjustable working distance adapter has been a versatile solution in both cases.[9]

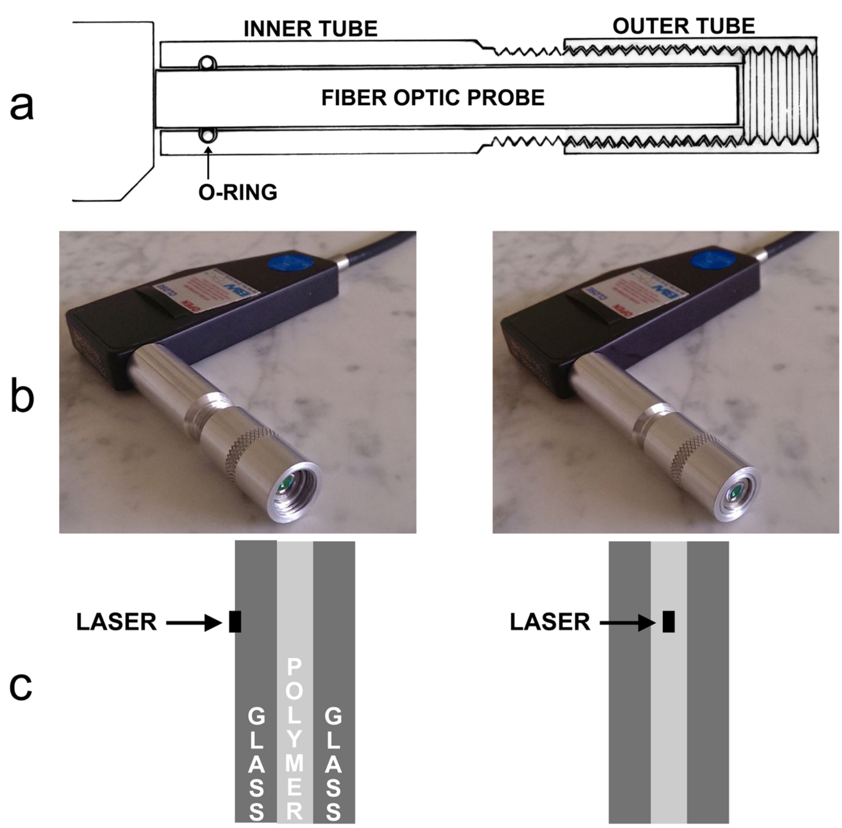

Figure 1. Adjustable working distance adapter. (a) Cross section view of adapter mounted on fiber optic probe, (b) photographs of adapter configured to analyze an object's surface (left) and maximum depth (right), and (c) schematic of how focal positions in (b) would apply to analysis of laminated glass.

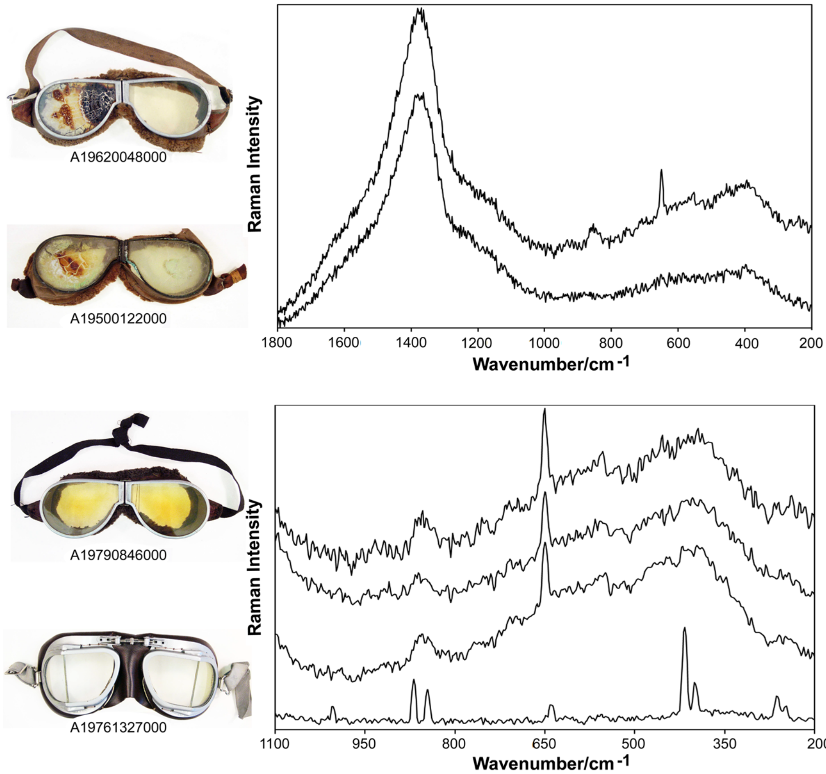

Figure 2. Raman spectra of aviator goggles in National Air and Space Museum collection. Upper spectral group shows two spectra collected at different depths into proper left lens of A19620048000, with lower spectrum representing the front glass pane and upper spectrum representing the polymer interlayer. Lower spectral group shows polymer interlayer of four goggle lenses (from top: A19620048000, A19500122000, A19790846000, A19761327000). Whereas upper three spectra are consistent with a World War I era formulation of cellulose nitrate plasticized with camphor, the lowermost spectrum suggests those goggles were manufactured later.

For this study, spectra were co-additions of 64 one-second scans collected at 785 nm excitation and 10 cm^{-1} resolution. The 1.5 m fiber optic assembly combines one excitation and one collection fiber into a single tubular probe that both focuses the excitation beam and collects the scattered light through a flat quartz window with antireflective coating, 5.9 mm working distance, and 85 μm focused analytical spot. The upper spectral group in Figure 2 shows two spectra collected at different positions in a lens from one set of goggles. The lower spectrum is of the glass pane with a broad spectral feature at 1000–2000 cm^{-1}. Although window glass is a relatively weak scatterer, its signature dominates both spectra because of the thickness of the glass panes relative to the polymer interlayer in these goggles. The upper spectrum shows peaks related to the interlayer; the most prominent of which are a sharp band at 650 cm^{-1} peak characteristic of the plasticizer camphor and a weaker, less defined band at 850 cm^{-1} that is consistent with cellulose nitrate but inconsistent with cellulose acetate (a less likely but plausible polymer from that era). There may be some contribution from camphor at 855 and 863 cm^{-1} as well.[9–11] Even though the depth resolution of the spectrometer and probe is too coarse to isolate the sub-millimeter thick polymer layer, the ability to finely position the focal point at the center of that layer allows its signal to be maximized relative to the surrounding glass. A second set of spectra illustrate that this formulation of cellulose nitrate plasticized with camphor was typical of laminated safety glass of the World War I period and was detected in most of the goggles with laminated lenses. An exception is Accession #A19761327000, the spectrum of which suggests a later fabrication date.

Discussion and conclusion

Improving interfaces between Raman spectrometers, artifacts, and operators is a central challenge for successful *in situ* analysis of cultural heritage objects. Transportable Raman spectrometers are a potential boon, but true portability and usefulness in a practical setting can be elusive. Handheld spectrometers are lightweight to carry but can become cumbersome and even unsafe for long analyses of fragile, awkwardly oriented objects. Tripods offer stability at some cost of portability and risk to the artifact. A fiber optic probe is lightweight, offers greater freedom of movement, and can be positioned in any orientation. For artifacts that are robust to direct contact, we present a hollow, adjustable working distance adapter that converts a fiber optic probe into a depth profiling device that is stationary relative to the artifact and excludes ambient light. The design is elegantly simple. The adapter contains no lenses, so optical quality and confocality are dictated by the fiber optic probe and spectrometer. The adapter's threaded aluminum tubes are finely machined, which allows for fine positioning of the focal point to maximize the Raman signal from thin layers. In addition to laminated glass, potential applications include gemstones, reverse glass paintings, face mounted photographs, and substances in transparent containers.

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