Journal of RAMAN SPECTROSCOPY

Received: 11 January 2014 Revised: 23 October 2014 Accepted: 27 October 2014 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/jrs.4618

Raman spectroscopic characterization of laminated glass and transparent sheet plastics to amplify a history of early aviation 'glass'†

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A novel, non-invasive study of goggles, flight helmets, airplane windows, and canopies in Smithsonian collections is the first known large-scale technical survey of historic aviation plastics and leverages the world's largest air and space collection as evidence of the materials and technologies used to create transparent plastic objects in the early-20th century. Transparent windows in these artifacts were analyzed with Fourier transform and portable dispersive Raman spectrometers to identify polymers and plasticizers present. The study demonstrates the potential of Raman spectroscopy to objectively and non-destructively measure historic plastic compositions, including formulations that have become obsolete. Data was interpreted in combination with archival research of historical documents to identify window materials including glass, laminated safety glass, and sheets of plasticized cellulose nitrate, plasticized cellulose acetate, and poly(methyl methacrylate). Results are contextualized into a coherent history of the role transparent plastics played in enclosing airplane cockpits. Published 2014. This article is a U.S. Government work and is in the public domain in the USA.

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Keywords: plastic; cellulose acetate; cellulose nitrate; PMMA; aircraft cockpit

Introduction

Early aviation design incorporated the most innovative plastics available at the time, and examples of these technologies are represented in the Smithsonian National Air and Space Museum (NASM) collection. Particularly interesting, and unexplored until now, is the co-evolution of transparent sheet plastics and the enclosure of cockpits in heavier-than-air aircraft of the 1920s and 1930s. A novel, non-invasive study of goggles, flight helmets, airplane windows, and canopies in Smithsonian collections is the first known large-scale technical survey of historic aviation plastics and leverages the world's largest air and space collection as evidence of the materials and technologies used to create plastic objects in the early-20th century. The study relied heavily on Raman spectroscopy to non-invasively identify the polymers and plasticizers present in the artifacts' transparent windows.

Many of the artifacts studied date to the earliest years of transparent plastic sheets, when compositions were experimental, evolving, and often different from polymer formulations that are common today. For this reason analysis was combined with study of historical documents that describe the state of the art when the artifacts were manufactured. This combined approach showed that a range of plastic materials were used, including laminated safety glass and sheets of cellulose nitrate and cellulose acetate, all of which required low molecular weight plasticizers, and eventually poly(methyl methacrylate) (PMMA). These findings support our proposition that the enclosure of aircraft cockpits was made possible by and spurred innovation in transparent plastics.

Background

In 1903 the Wright Brothers made their first powered flight at Kitty Hawk in an open architecture aircraft. It has been estimated that the total weight of the Wright flyer including the pilot was a mere 625 pounds, and it was moved by an 8 horsepower engine.[1] The dangers of flying in the open were obvious as pilots could be pitched out of the plane and killed.[2] By 1920, airplanes were more streamlined, and pilots were given some protection from the slipstream and elements by covering the aircraft's skeletal frame with fabric and leaving an opening on top for the pilot's head and shoulders.[3] This would have improved an airplane's aerodynamics by directing the air around rather than through it, but the big hole on top was a significant source of drag. It also did little for pilot comfort and protection. These early *cockpits* were located behind the engine, and the pilot was pelted with wind, rain, ice, oil, and the occasional bird that happened into the propeller. All threatened the pilot's ability to see and maneuver the plane. Goggles and small windshields were a first defense, provided they did not fail.[4,5] In the ensuing decades, as planes carried heavier loads and flew faster, higher, and longer distances, the open cockpit would have become an engineering challenge, and yet cockpits were not enclosed consistently until the late 1930s.

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† *This article is part of the special issue of the Journal of Raman Spectroscopy entitled "Raman in Art and Archaeology 2013" edited by Polonca Ropret and Juan Manuel Madariaga.*

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The central problem was that the pilot needed to see out of the plane in order to fly, and we posit that through World War I suitable window materials did not yet exist. In 1903, the landscape of transparent window materials would have included glass and some polymers such as cellulose nitrate, gelatin, and shellac. A successful window would not add too much weight to the plane, be resilient against changes in pressure and temperature, and protect against impacts. Plate glass was inappropriate for its weight and tendency to shatter on impact into sharp shards that could lacerate and kill the pilot. If a 1/4″ thick pane of glass 1 foot square can weigh from 3 to 8 lbs, and enclosing an airplane conservatively might take twenty of these, the glass alone would add 60–160 lbs to the vehicle weight. For a sense of scale, this would have increased the weight of the Wright flyer by 10–26%. The carrying capacity of planes increased dramatically in the ensuing decades, but the weight of windows in the first decades was important.[6] Injury from broken glass also would have been a hazard, as experience showed with automobiles that were undergoing a similar evolution.[7,8] A plate glass enclosure would have been unsuitable for an airplane, where the stakes for crashes were much higher.[7–10] New materials with transparency, strength, and fracture behavior suitable for aviation were developed in the ensuing three decades by which time enclosed aircraft had become the norm.

Materials and methods

This study of aviation materials combined research of historical documents with visual examination, Raman spectroscopy, and some X-ray fluorescence spectroscopic (XRF) analysis of historic artifacts to create a timeline of window materials used in early aviation. Archival research helped with deciphering Raman spectra that were hard to interpret because the formulation has become obsolete or was a mixture.

Artifact survey and comparative materials

Eighty-seven aviator goggles, flight helmets, and aircraft windows in the NASM collection were examined, and many of these included more than one window or lens. Raman spectra were collected from 76 windows and lenses from 39 artifacts, and the remainder was identified visually. Artifacts are identified here by the 12-character object numbers assigned by the museum (i.e. A19720891000).

Raman spectra of artifacts were compared to spectra of known reference materials that were measured at the Smithsonian's Museum Conservation Institute (MCI) with a FT-Raman spectrometer. Of the reference materials, cellulose acetate (CAS 9004-35-7), diethyl phthalate (CAS 84-66-2), and poly(methyl methacrylate) (CAS 9011-14-7) were purchased from Scientific Polymer Products, Inc. (6265 Dean Parkway Ontario, New York 14519). Dimethyl phthalate (CAS 113-11-3, Aldrich number 525081) and triphenyl phosphate (CAS 115-86-6, Aldrich number 241288) were purchased from Sigma Aldrich (sigmaaldrich.com). The cellulose nitrate reference was an experimentally prepared dope that was cast at MCI in 1994. The reference spectrum for camphor ((+/−)-Camphor, 96%, CAS 21368-68-3, Aldrich number 148075) was obtained from a commercially available spectral library (HR Aldrich Raman library, Copyright 1996–2001, 2004 Thermo Electron Corporation for Nicolet Raman).

Raman analysis

Two Raman spectrometers were used. A research grade Fourier transform Raman spectrometer with 1064 nm excitation (FT-Raman) offered spectra with high spectral resolution and low fluorescence collected in a laboratory setting, while a portable dispersive instrument with 785 nm excitation was evaluated for analysis of artifacts that were challenging because of their fragility, shape, size, or location. Both instruments are owned by MCI.

A portable B&W Tek MiniRam II dispersive Raman spectrometer was the primary tool. It incorporates a 785 nm excitation laser, 1.5 m fiber optic probe with 85 micron analytical spot, and thermoelectrically cooled CCD detection. An adjustable working distance adapter (described elsewhere) was designed to facilitate analysis of laminated glass structures.[11] Spectra were a co-addition of 12–64 1 second scans across 160–3207 cm^{-1} at 10 cm^{-1} spectral resolution. The instrument was controlled and data were collected using BWSpec™ spectral acquisition software (B&W Tek, Inc.). When possible, goggles with colored or deteriorated plastic lenses that fluoresced under 785 nm light also were analyzed in the laboratory by FT-Raman using a NXR module coupled to a 6700 Fourier transform infrared spectrometer (Thermo Electron Corporation). The NXR module is equipped with a $Nd{:}YVO_4$ excitation laser that emits 1064 nm radiation, CaF_2 beam splitter, and a Peltier-cooled InGaAs detector. Analyses were conducted in an enclosed sample compartment, which restricted the artifacts that could be studied to those with suitable dimensions. Each spectrum was a co-addition of 1024–4096 scans across 100–3700 cm^{-1} and 2–8 cm^{-1} spectral resolution. Instrument control, data collection, and spectral interpretation were managed by OMNIC 7.2a software (Thermo Fisher Scientific). All analyses were performed *in situ* without removing samples from the artifacts. Laser power was chosen on a case-by-case basis to optimize spectral quality and minimize risk to the artifacts, which exhibited a wide range of energy tolerances that could not be predicted reliably from an artifact's appearance. In each case, the analyst started with the lowest laser power available and increased it carefully until a usable spectrum was achieved. No baseline correction or smoothing was applied to spectra.

X-ray fluorescence spectrometry (XRF)

Elemental analysis supplemented the Raman results and visual examination in some cases. XRF spectra were collected with two instruments that offer different sampling geometries: an ElvaX energy dispersive X-ray fluorescence spectrometer (ElvaTech) (X-ray tube with rhodium anode, Si-pin detector, 165 eV resolution) and a Bruker ARTAX micro-XRF spectrometer (X-ray tube with rhodium anode, silicon drift detector, 70 eV resolution).

Archival research

Trade literature, patents, company records, and published histories were mined for information about the evolution of goggles, airplane design and the enclosure of cockpits, and the technological history of laminated safety glass, cellulose nitrate, cellulose acetate, and PMMA.

Results

What at the outset was hoped to be a straightforward set of transparent, colorless plastic windows turned out to be more complex. The collection to which we had access included a range of glasses, laminated glasses, and plastic sheets. Furthermore, many were colored, chemically degraded, or otherwise damaged. Three artifacts did not have any lenses at all. Ultimately, 76 goggle lenses, visors, and windows from 39 artifacts were measured by portable dispersive and/or FT-Raman spectroscopy. Summarized results for

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the Raman analyses are provided in Table 1 (window materials that include polymers) and Table S5 (window materials that include polymers and/or glass).

Raman spectroscopy and XRF

Of 87 artifacts examined, 39 goggles had glass lenses that could be distinguished easily with the portable Raman spectrometer. Seven of these goggles were analyzed by Raman as a proof of concept, and the other 32 were identified visually. The priority of the research was to trace the evolution of plastic materials, so these glass lenses were given only cursory attention. One interesting discovery by XRF was the presence of ultraviolet-absorbing cerium compounds in the glass lenses of some World War II era eyewear (A19760039000, A19781761000, A19810332000, A20010495000, and A20050338000).

Ten sets of goggles had lenses of shatterproof laminated safety glass. These consist of two sheets of glass sandwiched on either side of, and adhered to, a thin (<1 mm) plastic sheet. The fiber optic probe of the portable Raman was customized with an adjustable working distance adapter in order to probe the polymer layers through the glass, and these results are described in detail separately.[11] Eight of these laminated glass goggles were a flat-paned style that was common during World War I (Fig. 1). Portable Raman spectra indicated that the interlayer in six of the eight was cellulose nitrate plasticized with camphor. The remaining two had a red-tinted interlayer that was highly fluorescent and could not be identified. The ninth pair of laminated glass goggles, a British Royal Air Force style (A19761327000), had a face pad of synthetic leather that suggests a later manufacture date, and a colorless interlayer in the lenses with a unique but unidentified Raman spectrum. The tenth, Japanese goggles with curved lenses that

Table 1. Results summarized by window material and fabrication date. Object numbers are permanent identifiers that are searchable through NASM.

Window/lens material per Raman	Object number	Artifact type	Windows/lenses analyzed	Fabrication date
Plasticized cellulose nitrate sheet				
CN + camphor	A19250008000	Airplane window	1	1924
Laminated safety glass				
Laminated safety glass, CN + camphor	A20090121000	Aviator goggles	1	Circa 1920–1930s
Laminated safety glass, CN + camphor	A19500122000	Aviator goggles	1	Style consistent 1914–1918
Laminated safety glass, CN + camphor	A19620048000	Aviator goggles	2	Style consistent 1914–1918
Laminated safety glass, CN + camphor	A19790846000	Aviator goggles	1	Style consistent 1914–1918
Laminated safety glass, CN + camphor	A19910095000	Aviator goggles	1	Style consistent 1914–1918
Laminated safety glass, fluorescent unidentified interlayer	A19772777000	Aviator goggles	2	Style consistent 1914–1918
Laminated safety glass, fluorescent unidentified interlayer	A20000878000	Aviator goggles	1	Style consistent 1914–1918
Laminated safety glass, unidentified interlayer	A19603332000	Aviator goggles	1	Circa late-1930s–1945
Laminated safety glass, CN + camphor	A19540007000	Aviator goggles	1	Uncertain
Laminated safety glass, CA + DMP	A19610112000	Airplane window	1	1938
Laminated safety glass, unidentified interlayer	A19761327000	Aviator goggles	1	Uncertain
Plasticized cellulose acetate sheet				
CA + DEP + DMP + TPP	A19720891000	Aviator goggle lenses	8	Post 1943
CA + DEP + DMP + TPP	A19810020000	Aviator goggle lenses	3	Post 1943
CA + DEP + DMP + TPP	A19810185000	Aviator goggles	1	Post 1943
CA + DEP + TPP	A19740180000	Aviator goggles	1	Post 1943
CA + DEP + TPP	T20051030000	Aviator goggles	6	Post 1943
CA + DEP + TPP	T20051031000	Aviator goggle lenses	13	Post 1943
CA + DMP + TPP, possibly DEP	A19970586000	Aviator goggles	1	Post 1943
CA + DEP + TPP, possibly DMP	A19880585000	Aviator goggles	1	Circa 1944–1956
CA + DEP + TPP, possibly DMP	A19950796000	Aviator goggles	1	Post 1974
TPP + herapathite (CA, DEP likely)	A19910412000	Aviator goggles	3	Post 1943
CA + TPP (or similar compound)	A20050053000	Aviator goggles	2	Uncertain
Poly(methyl methacrylate) Sheet				
PMMA	A19602082000	Airplane canopy	3	1944
PMMA	A19600324000	Airplane canopy	3	1945
PMMA	A19781335000	Flight helmet	1	Circa1956
PMMA	A19731430000	Flight helmet	1	Circa 1960
PMMA	A19810003000	Flight helmet	2	Circa 1960
PMMA	A19800018000	Flight helmet	2	Circa 1965
Poly(vinyl chloride) sheet				
PVC + dioctyl phthalate	A20060135000	Jump goggles	1	Circa 2004

CA = cellulose acetate, CN = cellulose nitrate, DEP = diethyl phthalate, DMP = dimethyl phthalate, PMMA = polymethyl methacrylate, PVC = polyvinyl chloride, and TPP = triphenyl phosphate.

Figure 1. World War I era aviator goggles with shatterproof glass lenses laminated with a mixture of cellulose nitrate and camphor. The uneven darker tint at the center of the lenses is discoloration related to age.

date stylistically to World War II (A19603332000), also had a unique, unidentified interlayer spectrum.

Among the goggles and helmet visors with plastic lenses, three polymers were identified: cellulose acetate, PMMA, and polyvinyl chloride. Sixteen goggles were in the B-8 style, characterized by a one-piece rubber frame and a single mask-like lens (Fig. 2). The lenses were mass produced and designed to be interchangeable. Several of these goggles had multiple lenses, in a variety of tints, for a total of 47. Thirty-eight of these lenses were identified by Raman as cellulose acetate plasticized with a combination of diethyl and/or dimethyl phthalate and triphenyl phosphate, and a characteristic spectrum is shown (Fig. 3, Table S1). Cellulose acetate polymer compounded with one or more low molecular weight phthalates and triphenyl phosphate was a common formulation for plastic sheets and injection-molded objects from the 1930s onward, and typical Raman spectra have been described by Tsang et al.[12,13] These four compounds often can be discerned from a Raman spectrum even though many peaks overlap. For undegraded, plasticized cellulose acetate artifacts in the current study, Raman spectra could be translated as follows. Diagnostic peaks for the cellulose acetate polymer are 2939, 1435, 1379 (with shoulder at 1363), 910, 604, and 513 cm^{-1}. The carbonyl stretches at 1738 cm^{-1} in pure cellulose acetate and 1728 and 1725 cm^{-1} in dimethyl and diethyl phthalate, respectively, tend to merge into an intermediate value when these substances are compounded into a plastic. Diagnostic peaks common to diethyl and dimethyl phthalate that do not overlap with cellulose acetate or triphenyl phosphate are 1601, 1581, 1041, and 403 cm^{-1}. Dimethyl phthalate can be distinguished by the presence of additional peaks at 2844, 820, and a shoulder at 393 cm^{-1} and the absence of peaks at 866, 848, and 351 cm^{-1}. The converse is true for diethyl phthalate. For triphenyl phosphate, breathing of three benzene rings gives rise to a strong signal at 1007 cm^{-1}. Other characteristic peaks of triphenyl phosphate compounded with cellulose acetate include 1593, 1232, and 933, a partially shifted peak that spans from 726 to 719, and 617 cm^{-1}. Peaks typical of pure triphenyl phosphate crystals in the 270–170 cm^{-1} range are not diagnostic when the substance is dissolved in undegraded plastic.

Figure 2. M-1944 goggle (1974), a version of the B-8 goggle that became popular during World War II, consists of a molded rubber frame and a one-piece, interchangeable plastic lens.

Spectra of colorless lenses tended to be simpler to interpret due to lower fluorescence backgrounds, but this was not always the case. In most instances, colored lenses (yellow, orange, red, green, and blue) exhibited fluorescence at 785 or 1064 nm excitation, but the strongest peaks of the polymer and/or a plasticizer usually could be discerned at one of these wavelengths. Lenses that contained polarizing media, imprinted 'Polarizing' along the upper edge, were highly fluorescent at both laser wavelengths. Detection of iodine in these lenses by XRF suggests the polarizing medium may be herapathite (iodoquinine sulfate) crystals.[14]

Four American flight helmets that date from circa 1956 to 1965 were shown to have visors of PMMA using the portable Raman system (Figs. 4 and 5, Table S2). Peaks at 1730, 1450, 1122, 985,

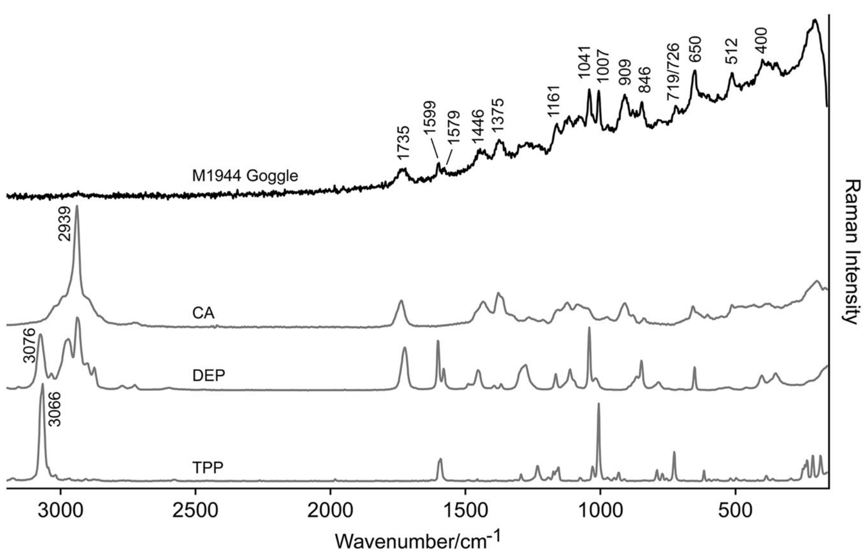
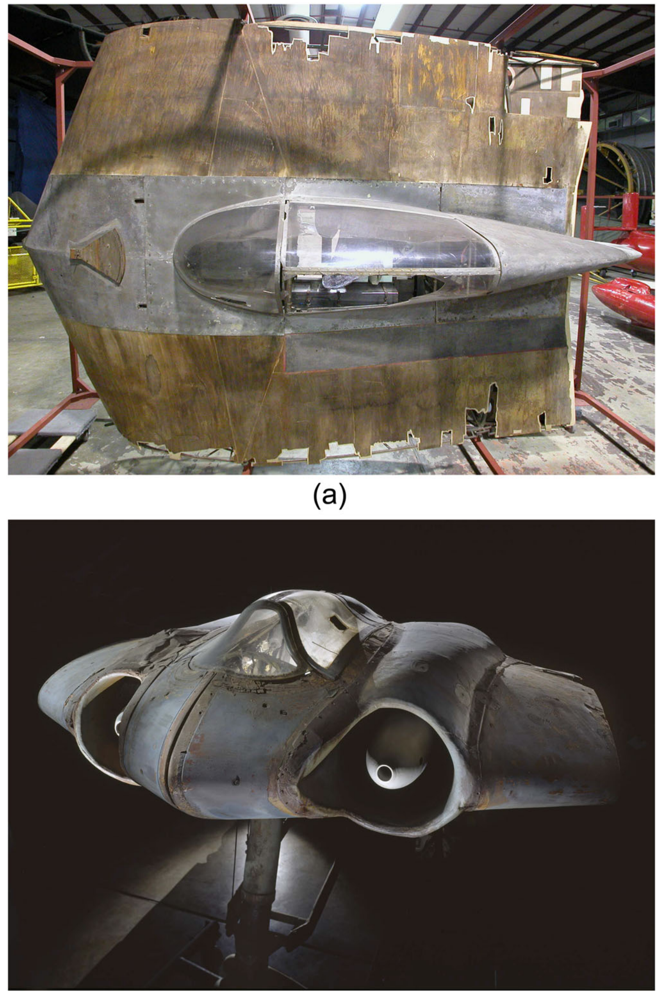


Figure 3. (From top) Raman spectrum of lens of M-1944 goggle (1974) collected with the portable instrument, compared to reference spectra of its constituent compounds, cellulose acetate, diethyl phthalate, and triphenyl phosphate, collected with the FT-Raman.

Figure 4. United States Navy Type HGU-20/P flight helmet (Photo: Smithsonian National Air and Space Museum (NASM 2011-00518)).

966, 812, 600, 559, 484, 364, and 297 cm^{-1} were visible consistently with a co-addition of 12 1 second scans. Three visors were tinted, and the colorant was not identified, but this may be the source of unidentified peaks at 639, 537, 520, and 416 cm^{-1} in the spectrum of A19800018000 (Fig. 5, Table S2). One set of goggles worn by the United States Army Parachute Team ‘Golden Knights’ (A20060135000, circa 2004) was constructed of a sheet of polyvinyl chloride plasticized with a phthalate plasticizer, most likely dioctyl phthalate. The one-piece lens was framed by colorless clear tubing made of the same compounds but with a higher concentration of the plasticizer. A set of survival goggles (A19750266000), still sealed in its original polyethylene bag, had lenses that fluoresced strongly under 785 nm excitation, and could not be identified. However, the transparent package (polyethylene) and nylon headband were identified with the portable instrument.

Of the four airplanes studied, the window from the 1924 Douglas World Cruiser ‘Chicago’ (A19250008000) was identified by FT-Raman as a sheet of cellulose nitrate plasticized with camphor (Figs. 7 and 8, Table S3). Camphor is the stronger Raman scatterer,



(a)

(b)

Figure 6. Two experimental German aircraft from World War II that feature transparent canopies of PMMA: (a) Horten H III h (1944), and (b) Horten H IX V3 (1945). (Photos by (a) Dane Penland (NASM 2012-01189) and (b) Eric Long (NASM 2000-9339), Smithsonian National Air and Space Museum).

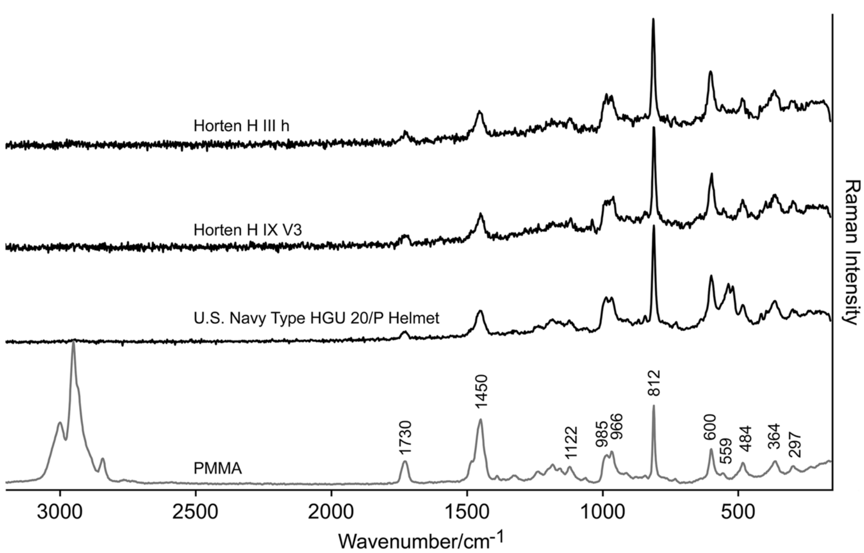


Figure 5. Raman spectra of canopies of two experimental German aircraft and the visor of a United States Navy flight helmet were measured with a portable Raman instrument and identified as PMMA. (Spectra from top to bottom) Horten H III h (1944), Horten H IX V3 (1945), United States Navy Type HGU-20/P protective flying helmet (1965–1971), and a FT-Raman reference spectrum of PMMA.

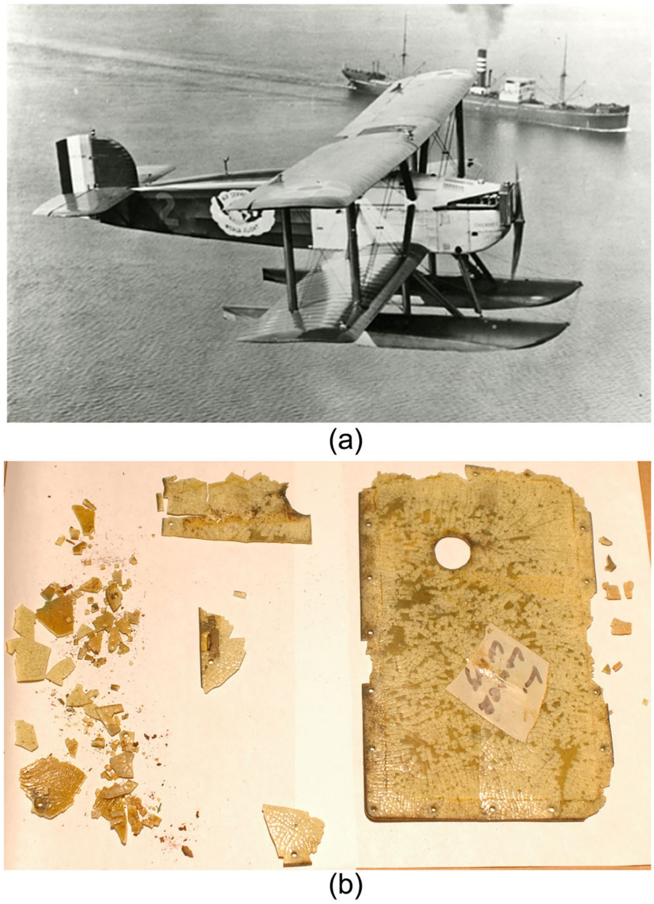


Figure 7. (a) Douglas World Cruiser 'Chicago' (1924) and (b) recent photograph of a disintegrating utility window identified by Raman as a mixture of cellulose nitrate plasticized with camphor (Historic photograph: Smithsonian National Air and Space Museum NASM 88-7415).

and its sharp peak at 652 cm^{-1} is the most prominent of the spectrum. This was also the diagnostic peak for cellulose nitrate interlayers in laminated glass, along with a weak cellulose nitrate signal at 850 cm^{-1}.[11] In the 'Chicago' window spectrum 37 camphor peaks are visible, plus the carbonyl stretch at 1743 cm^{-1} which is shifted to lower wavenumbers (1732 cm^{-1}) in the compounded plastic. A comparable reference spectrum and interpretation was published by Paris and Coupry in 2005, although we would assign the peak at 393 cm^{-1} to camphor rather than cellulose nitrate.[15] Features of cellulose nitrate also are present in the 'Chicago' window spectrum, with defined peaks at ~1647, 1373, 1284, 1120, and 850 cm^{-1}, but in general the cellulose nitrate contribution serves more to fill out the shape of peaks groups in which the camphor signal is more obvious.

A side window on the Sikorsky JRS-1 (A19610112000, fabricated in 1938) was identified as laminated safety glass with a cellulose acetate interlayer plasticized with dimethyl phthalate (Figs. 9 and 10, Table S4). The transparent canopies of the German experimental aircraft Horten H III h (A19602082000, fabricated in 1944) and Horten H IX V3 (A19600324000, fabricated in 1945) are PMMA (Figs. 5 and 6, Table S2).

Proposed historical timeline

Patents and trade literature of the time combined with Raman spectral data of NASM artifacts support our hypothesis that the development of transparent window materials was a rate determining factor in the movement toward enclosed aircraft along with the development of more powerful engines.

As described above, plate glass was inappropriate for early airplane windows because of its weight and tendency to shatter. Plastic sheets of that time would have offered the advantage of light weight but would seem unlikely to have had great success as windows because of their poor resilience to impact and pressure changes. However, the artifact record shows that cellulose nitrate windows were used in aircraft. The Douglas World Cruiser 'Chicago' is one of a set of four planes that flew around the world in 1924 and was acquired by NASM soon after (Fig. 7).[16] The cockpit was open, but some small utility windows on the wings presumably allowed for inspection of the equipment. One of these utility windows that had deteriorated severely and was removed from the airplane was analyzed for this study and identified as cellulose nitrate plasticized with camphor (Fig. 8). This is the classic formulation commonly described by the trade names Celluloid, Parkesine, and Xylonite.[17] Its chemical instability, which can manifest itself in the yellowing, opacification, and *crizzling* (a term used by art conservators to describe a pattern of fine cracks, usually in chemically unstable

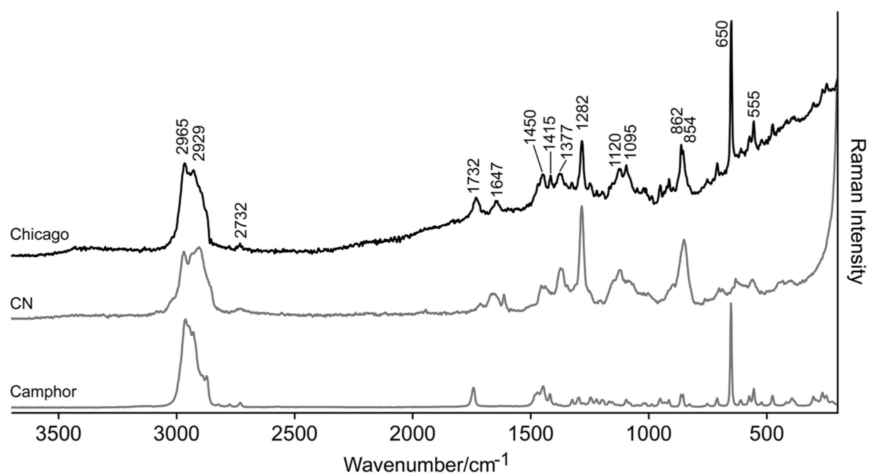


Figure 8. (From top) Spectrum of utility window from the Douglas World Cruiser 'Chicago' and reference spectra of its constituent compounds, cellulose nitrate and camphor, all measured by FT-Raman.

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Figure 9. Sikorsky JRS-1 amphibious aircraft (1938). (Photo by Dane Penland, Smithsonian National Air and Space Museum (NASM 2012-01396)).

glass, that renders the material dull and less transparent) exhibited in Fig. 7b, was well known by the 1920s, and it is a long-term stability problem in Smithsonian collections.[11] Despite the window's degraded state, its Raman spectrum is easily comparable to the reference spectra.

Cellulose nitrate also was used in windows as a laminating layer in shatterproof safety glass. This technology remains the industry standard for windshields in airplanes and cars today although the polymer interlayer has evolved. The invention of safety glass typically is attributed to French chemist Edouard Benedictus who developed and patented 'Triplex safety glass,' a laminate composed of a sheet of cellulose nitrate plastic adhered with gelatin between two glass plates, in around 1910.[18–24] In fact, the earliest patent for laminated safety glass for automobile windows was issued to John Crewe Wood in England in 1905.[25] Benedictus' first patent shows his appreciation of safety glass' great potential in a broad range of applications that have since become reality.[10,20] His composite glass was intended for windows and windshields in vehicles including "automobiles, cabs, carriages, omnibuses, railway carriages, boats, and the like," though aircraft were not specified at that early date.[20] He also noted that his glass could be used for windows with "quite original effects" by coloring or otherwise ornamenting the cellulose nitrate or glass.[20]

Because Triplex required non-standard thicknesses of flat, defect-free glass, and a multi-step manufacturing process conducted in cleanroom-like conditions, it was much more expensive than window glass, and this slowed its adoption.[9,21] World War I provided a major incentive for its development into "airplane and automobile windshields, bulletproof glass for tanks, glass for submarines, battleship-bridge windows, and eye blanks for gas masks and aviators' goggles."[10] In particular, lenses for eye protection made economic sense because of their small dimensions. They were adopted for civilian automobile driving and aviation, and were specified by the United States War Department for pilots in 1917.[26] In the NASM collection, laminated safety glass is found in aviator goggles of the World War I period and airplane windshields, and a cellulose nitrate/camphor formulation was identified by Raman in the majority of those studied.[11] The fact that the lenses are laminated suggests that protection of the eyes from impacts was a concern. This and other details such as a warm, fleecy face pad (A19540007000) are consistent with open cockpit flying. Other interesting features of these goggles include tinted interlayers (e.g., cyan (A20090121000), amber (A19772777000, A20000878000), and two-tone blue and clear (A19910095000)), as suggested by Benedictus and intimates the importance of being able to see in a range of lighting conditions.

By the 1920s the shortcomings of cellulose nitrate were well known, and safety glass interlayers were known to deteriorate within a few years of use.[10,21,27] Several goggles in the NASM collection exhibit typical discoloration, shrinkage, and separation of the interlayer (A19500122000, A19620048000, A19790846000, and A20090121000), and a mild example is shown in Fig. 1.[11] In time the manufacturing process was modified to include sealing the edges of the laminate sandwich to prevent infiltration of moisture to the plastic layer and slow degradation, but ultimately cellulose nitrate was phased out in favor of cellulose acetate, a polymer that was developed as a non-flammable substitute in the late 1920s.[10,21,28–31] Cellulose acetate was adopted for many of the same applications, including as a safety glass laminating layer that was more chemically stable than its predecessor.[28,29,32]

Cellulose acetate laminated glass was not encountered in the NASM goggle collection but was found in the side windows of the Smithsonian's United States Navy JRS-1, a twin engine amphibious aircraft built by the American company Sikorsky Aircraft in 1938 (Fig. 9). It is the one airplane in the NASM collection that

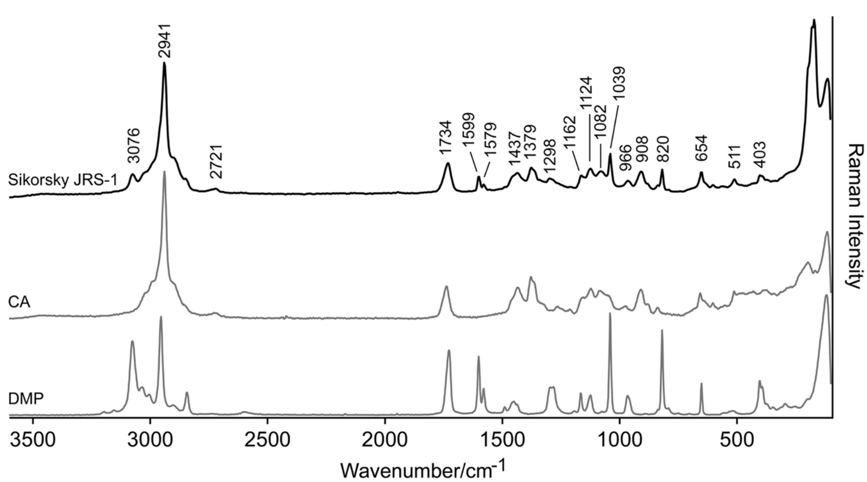

Figure 10. (From top) Spectrum of the laminated safety glass interlayer from a round side window of the Sikorsky JRS-1 (1938), and reference spectra of its constituent compounds, cellulose acetate, and dimethyl phthalate, all measured by FT-Raman.

was stationed at Pearl Harbor on 7 December 1941 and is the sole surviving aircraft of its kind.[33] Raman spectra confirmed that the round side windows of this transport are laminated safety glass with an interlayer of cellulose acetate plasticized with dimethyl phthalate (Fig. 10). This would have been a late example of that interlayer, which underwent a major change the following year. One drawback of cellulose acetate laminated safety glass was its rigidity.[10] When struck by an object, like a person's head, the glass would break but not yield, and this caused head trauma. This public health problem was taken on in 1939 by a collaboration of chemists, engineers, and manufacturers from E. I. du Pont de Nemours and Company, Pittsburg Plate Glass Company, Libby-Owens-Ford Glass Company, Monsanto Chemical Company, and Carbide and Carbon Chemicals Corporation who spent $6 million to develop an ideal safety glass laminating layer.[9,34] Their polyvinyl butyral resin (PVB) was stable chemically, dimensionally, and mechanically; had a broad glass transition temperature range that accommodated cold and hot climates; possessed superior adhesion qualities; and was flexible and easy to work with. When a projectile hit this safety glass it would deform (and transfer the force of impact into the window), but the large fragments would not detach. This resin remains an industry standard today. PVB safety glass was not identified in the artifacts available for this study though the authors assume it is common in laminated glass windshields after 1939 and that the window of the Sikorsky JRS-1 is an example of a technology in its waning years.

By 1938 another sea change in airplane window glazing was underway. In the 1930s, German chemist Otto Rohm and his associate Walter Bauer experimented with PMMA as a potential safety glass interlayer. They poured the monomer directly between two sheets of glass and polymerized it in place with light. However, instead of cementing the two panes together as intended, the polymer separated cleanly from the glass in a strong, solid, transparent, optically clear, glass-like material that could be cast, sawed, bent, and machined. They quickly recognized its potential in aircraft glazing.[35–37] A full-page advertisement extolling its light weight, hardness, impact strength, perfect transparency, weathering, and ease of forming appeared in the July 1937 issue of the New York based journal, *Aero Digest*, where it was placed prominently opposite the table of contents.[35] Windows, gun-turrets, observation blisters, and nose cones of PMMA soon proliferated and became popular symbols of World War II aeronautic technology.[37,38] Rohm and Haas had operations in Germany and the United States, and their Plexiglas was used in both markets.[32] Raman analysis shows that PMMA was the plastic sheet of transparent canopies on two experimental 'Horten' German jet airplanes constructed during World War II; the Horten H III h and Horten H IX V3 each feature a PMMA canopy constructed in three parts (Fig. 6). PMMA also was used for the visors on four flight helmets used by the United States Navy and Air Force in the 1950s through 1970s (A19731430000, A19781335000, A19800018000, and A19810003000) (Fig. 4).

Aviation glazing was a large potential market for plastics, and a range of competitors came on the market around this time. Cellulose acetate, polyvinyl chloride, cellulose nitrate, and laminated safety glass options appear in *Aero Digest* beginning in 1938.[39] Unpublished research and development reports from the Celluloid Manufacturing Company show that company was actively trying to compete in the aircraft window market by 1943 with their Aero Quality Lumarith cellulose acetate sheet, the main competitors for which appear to have been Rohm and Haas' Plexiglas and Vinylite polyvinyl chloride from Carbide and Carbon Chemicals Corporation. Neither Lumarith nor Vinylite has been encountered yet in the NASM collection.

Enclosed cockpits were the norm by the late-1930s, and transparent plastic sheet certainly revolutionized their construction. However, these soft materials did not meet all window glazing needs. Laminated safety glass continued to play an important role in windows that required protection from bird strikes and other projectiles, abrasion resistance, and activities that required optical precision such as aiming weapons or focusing cameras.

With the enclosure of cockpits, goggles shifted from the World War I style with laminated safety glass lenses to metal-framed goggles with ground glass lenses, rubber-framed goggles with one-

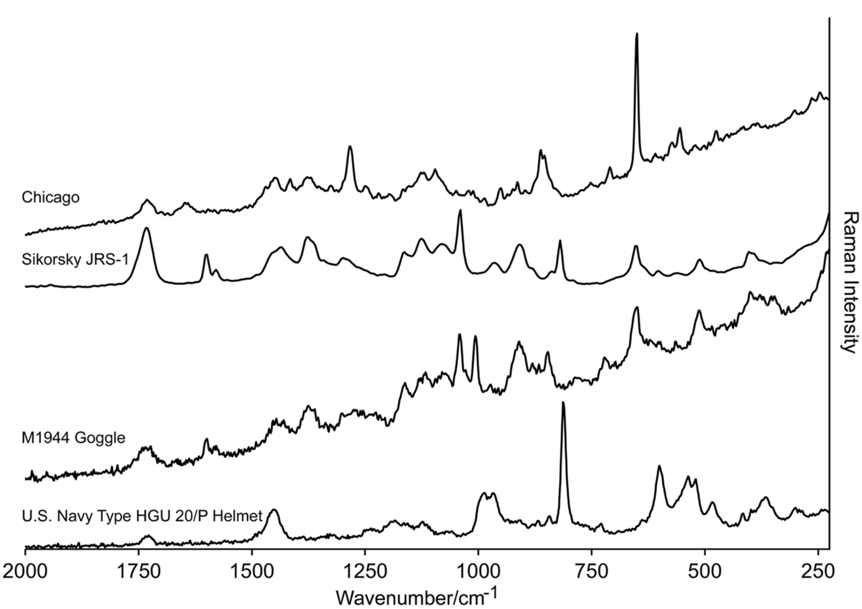

Figure 11. Raman spectra of four window materials used in aviation. (From top) cellulose nitrate sheet plasticized with camphor from Douglas World Cruiser 'Chicago' (FT-Raman), laminated safety glass interlayer of cellulose acetate and dimethyl phthalate form Sikorsky JRS-1 (FT-Raman), cellulose acetate sheet with diethyl phthalate and triphenyl phosphate from M-1944 goggle lens (portable Raman), and PMMA sheet from the visor of a United States Navy flying helmet (portable Raman).

piece plastic lenses, and sunglasses, all of which suggest that concern about eye protection had been supplanted by optical performance and manufacturing ease. Study of the NASM collection showed that glass and plastic lenses were offered a variety of tints to suit different lighting conditions. Some higher tech light filtering solutions included ultraviolet-absorbing cerium compounds in glass (A19760039000, A19781761000, A19810332000, A20010495000, and A20050338000) and polarizing plastic lenses impregnated with aligned herapathite (iodoquinine sulfate) crystals (A19910412000).[14] The biggest advance in flying goggles of the World War II period was the Polaroid company's introduction of the rubber-framed B-8 google in 1943. The flexible frame offered a one-size-fits-all option for both aviators and ground crew, and one-piece mask-like lenses of cellulose acetate plasticized with low molecular weight phthalates and triphenyl phosphate maximized visibility and were easily exchangeable. A descendant of the B-8 goggle called the M-1944 is shown in Fig. 2.[40]

Discussion and conclusions

This work is significant for both Raman spectroscopy and the history of technology. From the perspective of the spectroscopy, the data shows that Raman is a valuable tool for identifying polymers, plasticizers, and other compounds encountered in plastic. As a result of this study, FT- and dispersive instruments now are used routinely to sort transparent and colorless plastics at Smithsonian and often can identify major components of intentionally colored or degraded material as well. This article provides spectra of naturally aged examples of historic cellulose nitrate and cellulose acetate formulations, and PMMA (Fig. 11). A portable spectrometer with 785 nm excitation and modified fiber optic probe facilitated analysis of historic artifacts by bringing the instrument to objects that are large, challenging to access, oddly shaped, or fragile.

As expected, fluorescence interference was a challenge for many artifacts, particularly plastics that are colored or contain polarizing media. Better spectra were obtained for some objects with a 1064 nm FT-Raman spectrometer, but the instrument is not portable and has an enclosed sample compartment, which limited the range of artifacts that could be analyzed. This finding underscores the potential for portable Raman spectrometers with NIR excitation. The FT-Raman was preferred for creating spectral reference libraries and studying multi-component formulations because of its spectral precision, adjustable resolution, and lower fluorescent background.

From a historical standpoint, synthetic polymers are one of the great discoveries of the last two centuries, and it is important that we record this history through study of our cultural heritage. Plastic technology evolved rapidly in the early 20th century, and experimentation with formulations and processing methods was common. In this article we have explored that evolution by looking at the symbiotic relationship between early plastics and aviation. While archival research offers a valuable view of what was available at the time, visual observation of artifacts aided by non-destructive Raman and XRF spectroscopies shows definitively what was used. Conversely, a spectrum can record an artifact's composition, but it may reflect a mixture that has become obsolete or forgotten, and include alteration products that form with age. A clear historical understanding of the technologies that were possible for a particular artifact is key for reliable spectral interpretation. For these reasons, it is vital that historical and scientific analytical approaches be applied to cultural heritage studies in unison.

Finally, this study of plastics in early aviation demonstrates a way in which Raman spectroscopy can be harnessed to further research that is significant to the field of history. Studies of cultural heritage benefit from a significant research question. Here, Raman spectra are interpreted in the broader context of an important technological evolution rather than as individual objects. These early window materials were so successful that we now take them for granted, but they solved vital public safety issues and are the origin of important descendant technologies including personal electronics (e.g. computers, tablets, mobile phones), structural laminated glass used in architecture, and explosion and projectile proof glass. Here we have demonstrated how Raman spectroscopy contributed to a preliminary but quite robust technological history.

Acknowledgements

This research was funded by the National Park Service and the National Center for Preservation Technology and Training (Grant # Mt-2210-10-NC-10). Its contents are solely the responsibility of the authors and do not necessarily represent the official position or polices of the National Park Service or the National Center for Preservation Technology and Training. The B&W Tek MiniRam II spectrometer was purchased with a generous gift from Judith Cherwinka. Gary Gordon of NASM and Don Williams, emeritus of MCI, fabricated two iterations of the adjustable working distance adapter. Marion Mecklenburg, emeritus of MCI, cast the cellulose nitrate sheet we used as a reference. Liz Garcia, Jennifer Stringfellow, Malcolm Collum, Lauren Horelick, Jeremy Kinney, and Ellen Folkama facilitated access to the NASM collections. Russ Lee, Chris Moore, Robert Koestler, Paula DePriest, Molly McGath, and Dawn Planas offered valuable discussion and analytical support.

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