Article: Blow it off: Moving beyond compressed air with carbon dioxide snow
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BLOW IT OFF: MOVING BEYOND COMPRESSED AIR WITH CARBON DIOXIDE SNOW

L. H. (HUGH) SHOCKEY JR.

ABSTRACT

Carbon dioxide snow cleaning has advanced significantly in recent years, making it an affordable and consumer-friendly surface cleaning method. The technology has been tested and used in critical cleaning applications, such as the removal of surface contamination during the production of silicon microchip wafers and precision optical lenses. Carbon dioxide snow cleaning is an emerging technology in conservation with the possibility of aiding in the cleaning of sensitive surfaces.

Robert Morris' molded plastic sculpture *Model*, 1967 was requested for loan from the Smithsonian American Art Museum's collection. As part of the loan process, the work was examined and a whitish surface haze was readily visible that disfigured the appearance of the work. After careful consideration, carbon dioxide snow cleaning was chosen as the treatment method to address the surface condition. Carbon dioxide snow proved to be an effective and efficient method of reducing the appearance of the disfiguring haze without bringing solvent or aqueous cleaning systems to the surface of the sculpture. The results from the cleaning of Robert Morris' *Model*, 1967 suggest that carbon dioxide snow cleaning may provide a useful tool for the conservator's toolbox with the potential to address cleaning problems and ongoing maintenance of objects with sensitive surfaces.

1. INTRODUCTION

The Smithsonian American Art Museum (SAAM) collects, exhibits, and loans works by American artists with works spanning the history of the United States. The museum actively loans works from its collection to disseminate knowledge of American art and artists. A request to borrow Robert Morris' *Model*, 1967 from the SAAM collection prompted examination of the work. *Model* is a molded plastic wall sculpture from a series of multiples in the style of the minimalist movement of the late 1960s. During initial examination, a white haze was apparent on the surface of the sculpture that detracted from the minimalist aesthetic of the work. Microscopic examination revealed that the haze was the result of small crystalline deposits on the surface of the polymer. To properly represent the artistic intent of the work during exhibition, the white disfiguring haze would need to be removed.

Several methods of removal were considered. Traditional mechanical surface cleaning posed the risk of scratching the smooth surface of the work. Aqueous or solvent cleaning could remove the material; however, it could also cause problems with the polymer's structure, potentially increasing its crystallinity. Carbon dioxide (CO_2) snow was also considered as a third possibility since the technique could provide the benefits of mechanical cleaning while reducing the potential for damage. After testing of these various methods, carbon dioxide snow was chosen to remove the crystalline deposits that caused the visible white haze.

1.1 CARBON DIOXIDE SNOW

Carbon dioxide snow is the single crystalline solid form of carbon dioxide. CO_2 snow should not be confused with commercially produced dry ice. Dry ice is the macro form of solid carbon dioxide found in pelletized forms that are millimeters in scale. By contrast, carbon dioxide snow crystals are micrometer (micron) size particles (Hill 1994, 36). Understanding the particle size is important since the primary cleaning mechanism of CO_2 snow is momentum transfer, whereby momentum is the relationship between mass and velocity (Cano 2001, 330). Carbon dioxide snow cleaning uses the low mass of the solid crystal at high velocity. Carbon dioxide snow's advantage over compressed air is due to the ability of the micron-sized snow particle to penetrate the turbulent air boundary layer that is approximately 3 microns thick and present on the surface of all objects in the atmosphere (Sherman 2007, 40). Penetrating this boundary with the physical particle allows for momentum transfer to displace surface soiling.

In addition to momentum transfer, several mechanisms are thought to contribute to the cleaning efficacy of CO_2 snow. These are the solvent effect that carbon dioxide has on hydrocarbon soiling, and the theoretical effects of temperature depression commonly referred to as "freeze-fracture" in the literature (Cano 2001, 331-333). The term "freeze-fracture" suggests freezing temperatures. However, anecdotal testing using a FLIR 320EX thermal imaging camera with the CO_2 snow jet directed at and impacting the lens revealed the lowest temperature to be 46.6°F (8.1°C), far from the freezing point of water (fig. 1).[1]

Fig. 1. The display screen of the FLIR unit showing the low temperature value of 46.6°F. The black spot on the screen is the CO_2 snow jet in direct contact with the instrument's lens. (Photograph by Shockey)

1.1.1 Making Snow

Presently, a limited number of methods produce carbon dioxide snow. The current technology of production incorporates a nozzle with specific internal geometry and a CO_2 source. The geometry of the nozzle and the type of source directly influence the efficiency of snow generation, the snow crystal size, and the size of the cleaning area (Cano 2001, 331). The most common nozzle geometries can be characterized as either single expansion or double expansion types (Sherman 2007, 44). While other designs exist, they lack the constant enthalpy conditions that allow them to be used with both CO_2 liquid and gas sources and lack efficiency in the generation of snow particles.

Either liquid or gaseous CO_2 can be used to generate CO_2 snow. Liquid source generation offers the advantages of producing great quantities of particle and large particle sizes; however, it also has the disadvantage of inefficient snow formation in comparison to source consumption. In addition, it has the potential to carry contaminates from the compressed gas cylinder solubilized by contact with the liquid CO_2. Gas source generation offers the advantages of low contamination, high efficiency in relation to source consumption, and production of a finely focused crystal stream; at the same time, it lacks the displacement ability of larger crystals and the large volume of crystals generated with a liquid source (Hill et al. 1999, 29-30).

With CO_2 snow cleaning, the efficiency of crystal formation can be enhanced with the addition of a moisture-displacing cover gas or warmed air (Sherman 2007, 46). A moisture-displacement gas can be integrated into the snow generation nozzle or can be supplied via a secondary system. The snow unit used at the Lunder Conservation Center is a purpose-designed dual gas unit that allows the moisture-displacement gas, or cover gas, to be delivered coaxially with the snow stream (fig. 2). Other moisture-displacing methods used in the conservation laboratory with CO_2 snow include a dry inert gas supplied non-axially or warm air from a hot air gun used to flood the surface to be cleaned. Nitrogen (N_2) is a good choice of cover gas since it is non-flammable, relatively inexpensive and is supplied dry in a compressed cylinder. The snow unit at the Lunder Conservation Center uses a dry nitrogen cover gas that can also be heated above room temperature via a temperature controlled in-line heated hose.

Fig. 2. Detail of the co-axial nozzle. The center hole in stainless steel is the CO_2 snow exit. The multiple holes in the white fluoropolymer are N_2 cover gas exits. (Photograph by Shockey)

1.1.2 Considerations for Choosing CO_2 Snow for Cleaning

The primary considerations for choosing CO_2 snow as a cleaning method are: (1) the type of soiling to be removed, (2) the surface to be cleaned, (3) the effect of temperature depression on the material to be cleaned, and, (4) the ability of the object to be cleaned to withstand the force of the CO_2 jet.

Research has shown that CO_2 snow cleaning is most effective for the removal of non-covalently bound particulate material from the surface of solid, minimally energy absorptive substrates (Hill 1994, 39; Sherman 2007, 42-43). As with all cleaning systems, the parameters for use can be pushed, but the efficiency and effectiveness will be impacted. For momentum transfer to be effective as a method of cleaning, the soiling to be removed must have a bond energy with the substrate that is weaker than the energy transferred by the snow particle (Hill 1994, 38-39). Surfaces that are minimally energy absorptive, that is, materials considered "hard" or "glassy," will be cleaned more effectively since the energy of the snow crystal will not be lost by absorption and dissipation into a "soft" surface (Sherman 2007, 50-52).

Thermal conductivity and the response of the material to be cleaned to temperature depression must also be carefully considered. Materials with high thermal conductivity have the potential to quickly condense atmospheric moisture on the surface if the temperature crosses below the dew point. Condensation can be mitigated with the use of a dry cover gas. Additionally, this gas can be further heated to manipulate the localized dew point (Cano 2001, 333). The temperature depression caused by the cold temperature of the CO_2 snow jet must be considered for materials that have critical glass transition (T_g) temperature points close to room temperature. Materials considered for cleaning with CO_2 snow must be able to withstand the force of the jet that delivers the snow crystals to the surface. Every CO_2 snow generation unit will have a different maximum jet velocity between 3 and 100 meters per second (m/s) (Sherman 2007, 44). The Lunder Conservation Center's CO_2 snow unit has a maximum recorded velocity of 46.9 m/s (fig. 3).

Fig. 3. Velocity testing in the conservation lab. The white CO_2 snow jet can be seen between the end of the nozzle and the entrance of the meter. (Photograph by Shockey)

Several additional factors are worth considering when evaluating the use of CO_2 snow as a cleaning method. These include: (1) the re-deposition of displaced soiling back onto the cleaned surface, (2) the generation of a static charge on the surface of some materials, (3) safety issues, and, (4) user experience.

As CO_2 snow is a momentum transfer and displacement cleaning method, the soiling material is ejected from the surface without an active capturing method, such as vacuum suction or air extraction. Consequently, the soiling particle will be deposited where it lands (Cano 2001, 334). There are several techniques that can be used to control this problem. Conscientious technique during cleaning is the first method of effective control. This consists of deliberately working from areas that have been cleaned toward areas that are soiled, often from the center of an object towards the outer perimeter. Ejected particulate soiling matter can be captured using sticky mats of various sizes available from clean room suppliers and by the use of a suction apparatus (i.e. a vacuum or fume extractor) placed on the far side of the blast direction.

The kinetic reaction of particulate removal from momentum transfer will have the secondary effect of elevating the potential energy on the surface of some material types (Cano 2001, 334). This becomes evident through increased static charge on the cleaned surface. This static charge can easily be mitigated with the use of an anti-static generator nozzle fitted to an air supply. The nozzle is usually a dedicated unit utilizing a compressed gas or ambient air source. The snow unit at the Lunder Conservation Center has an in-line, anti-static unit that is part of the nitrogen cover gas supply.

As with any treatment method, proper safety should be considered. Carbon dioxide snow presents several possible safety concerns: (1) it creates a CO_2 rich environment that can cause asphyxiation in an enclosed space without air exchange, (2) it can produce flying debris at elevated velocities requiring both proper eye protection and inhalation protection, (3) the high velocity jet can produce high decibel level noise, particularly when it encounters changes in topography on a surface, which requires the use of hearing protection (Cano 2001, 335-336).

User experience contributes significantly to the speed and quality of cleaning. An experienced user can minimize the occurrence of condensation and re-deposition of soiling material onto the cleaned surface and can quickly judge how effective CO_2 snow will be on an object to be cleaned.

2. ROBERT MORRIS' *MODEL*, 1967

Robert Morris's *Model* from 1967 is one in a series of 200 molded sculptures of cellulose acetate butyrate (CAB) and is 23 1/8 x 19 3/8 x 1 1/4 inches (58.7 x 49.1 x 3.1 cm) in dimension (fig. 4). The sculpture is the monochrome green color of the polymer. Overall, it is rectangular in shape with a raised circular form in the middle, reminiscent of a doughnut or life-preserver ring. Two of the four edges, one long and one short, have two concave depressions that correspond, spatially and conceptually, to the raised center ring. The signature and number are engraved into the polymer matrix on the back along the lower turned edge of the sculpture. The cellulose acetate butyrate substrate is a continuous sheet with a thickness of 2 mm. Yvonne Shashoua of the National Museum of Denmark identified the polymer composition from thin samples using Fourier Transform Infrared Spectroscopy (FTIR).

When examined as part of the loan request process, the sculpture was found to be in a structurally stable condition. The primary condition issue identified was the sculpture's aesthetic appearance. Surface dirt and grime, an overall white haze, and both fine and deep surface scratches impacted the appearance. The most visually significant of these conditions was the presence of the whitish haze on the surface. Examination of the haze under the stereo binocular microscope revealed that the haze was composed of small crystalline deposits that appeared smooth on their surfaces (fig. 5). Raking light examination under magnification showed that the deposits were raised above the surface. While the deposits were scattered over the surface, heavier concentrations were evident around changes in surface topography inside and outside of the central ring form. Samples of the deposits were taken from several areas on the surface using sterile cotton swabs and packaged in glass vials. These samples were sent to Yvonne Shashoua for analysis. Identification of the composition of these deposits has thus far been inconclusive.

Fig. 4. Before-treatment image of the sculpture. The streaks in the center are indicative of the white deposits. (Photograph by Shockey)

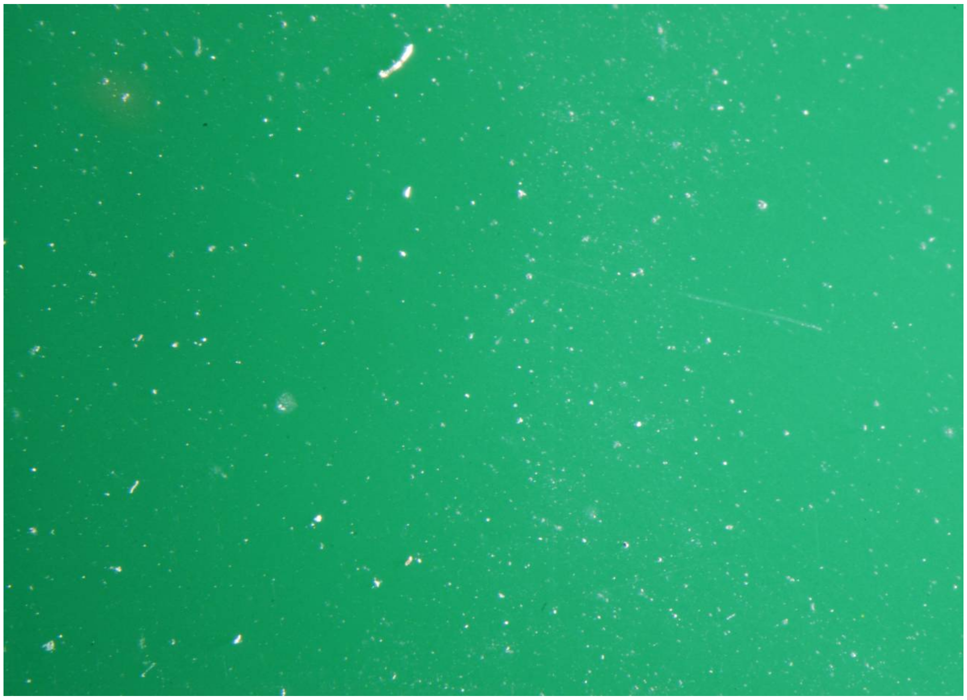

Fig. 5. The surface of the sculpture at 60x showing the crystalline appearance of the white deposits (Photograph by Shockey)

2.1. TREATMENT OF *MODEL*

The treatment of Robert Morris's *Model* was undertaken to correct the aesthetic deficiency of the sculpture, making it suitable for exhibition as an example of high minimalist art (fig. 6). In approaching the treatment it was necessary to consider the potential impact of cleaning on the polymer matrix. Without clear confirmation of the composition of the white deposits on the surface it was hypothesized that it could be plasticizer that had migrated out of the CAB polymer matrix. Testing indicated that aqueous cleaning might be possible since the white deposits appeared to be water soluble. The use of an organic solvent system was not pursued due to the potential for damage to the polymer. Consideration was given to current research on the conservation treatment of plastic materials; this research suggests complete removal of migrated plasticizer and other modifiers from the surface of a polymer may contribute to additional migration, further altering the internal composition of the plastic (Shashoua 1998, 175, 209). With this in mind, CO_2 snow was considered and tested.

The results of the test showed that the deposits were reduced to the point of invisibility under normal viewing conditions (fig. 6), but microscopic remnants were visible when examined under magnification (figs. 7-8). Careful consideration was given to the possible effects of temperature depression on the polymer. Testing was conducted with the CO_2 unit to determine the low-end temperature range of the jet using a Fluke 561 HVAC Pro non-contact infrared thermometer. The lowest surface temperature recorded during the momentary blast of the CO_2 snow jet on the surface was 47°F (8.3°C) with a rapid return of the surface to ambient temperature. Potential damage from the force of the jet was also considered. This concern was mitigated with the use of a polyethylene foam insert on the reverse of the sculpture to prevent possible deformation of the polymer during cleaning.

With these concerns addressed, and with the knowledge that CO_2 snow cleaning could provide a dramatic improvement to the aesthetic appearance of the work without entirely removing the deposits, the decision was made to move forward with snow cleaning as the treatment method. The pre-existing physical damage to the surface in the form of scratches and abrasions was deemed aesthetically acceptable since invasive alteration and removal of original material from the surface by polishing would have been the only treatment option, and research has shown that such surface alteration can have a negative impact on the long term preservation of the plastic material (Shashoua 1998, 213).

Fig. 6. After-treatment image of sculpture with no apparent surface deposits (Photograph by Shockey)

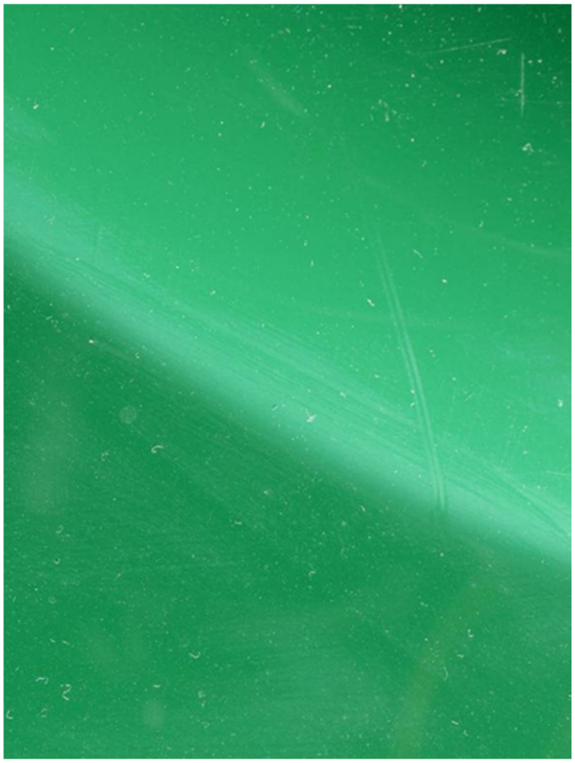

Fig. 7. Appearance before cleaning at 10x
(Photograph by Shockey)

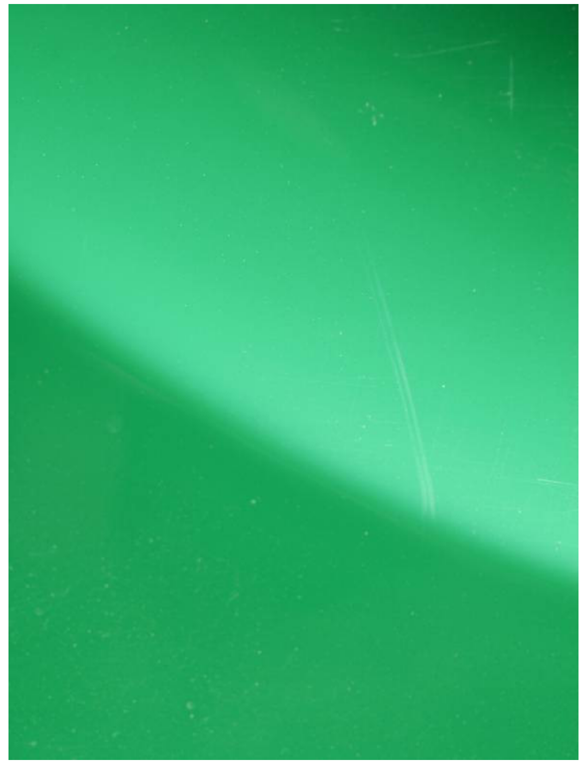

Fig. 8. Appearance after cleaning at 10x
(Photograph by Shockey)

The removal of the deposits was approached in a systematic manner. With the foam support in place, the sculpture was placed face-up on the treatment table with a Nederman fume extraction trunk on the far side of the treatment area for particulate collection. With the nitrogen cover gas activated, the CO_2 snow nozzle was directed at the surface. A broad circular motion was made with the nozzle at roughly 90 degrees to the plane of the object, and a sustained blast of CO_2 snow, emitted approximately 12 inches (30.5 cm) above the sculpture, was used to "pre-chill" the surface. This technique has been found to assist in mitigating the potential for condensation. The nozzle was brought closer to the surface at the center of the sculpture with an angle of 45 degrees or less to the surface. Intermittent blasts of the CO_2 snow jet were used for active cleaning. With this technique, removal of the white deposits commenced. A side-to-side sweeping action was used in addition to the intermittent snow blasts. Beginning in the center, cleaning continued with a steady movement outward toward the edges of the sculpture. Care was taken during cleaning to overlap each sweep of the CO_2 snow jet with the previous when moving the cleaning front forward (i.e. as when spray-painting a surface). The sculpture was moved and rotated on the treatment table to maintain alignment with the fume extractor on the far side and the direction of the blast. Areas needing additional attention were approached in the same manner as the overall cleaning. A final overall pass was executed from the center outward to ensure all residual debris was removed from the surface. As a follow-up to the final pass, the anti-static generator was activated in the nitrogen supply line and a stream of deionized nitrogen was passed over the surface in broad sweeping strokes with the nozzle held at approximately 90 degrees to the surface. The total active treatment time for the *Model* was less than one hour and resulted in significant visual improvement of the work.

2.2. EVALUATION OF CO_2 SNOW TREATMENT

To compliment the perceived aesthetic improvement of the work following treatment with CO_2 snow, Yvonne Shashoua provided information regarding the treatment's effect on the structure of the polymer substrate. To facilitate this analysis, the reverse of the sculpture was cleaned in the same manner as the front. Ms. Shashoua provided instructions for removing thin-section samples from the plastic substrate for testing the effects before and after cleaning. Following these instructions, SAAM conservator L.H. (Hugh) Shockey, Jr. removed the thin-section samples from the reverse of the sculpture with a sharp micro chisel and packaged them for mailing. Ms. Shashoua ran attenuated total reflectance (ATR) at a resolution of 4 cm^{-1} over 20 scans using a Durasampl IR ATR with diamond crystal on the thin-section samples, one before treatment and one after treatment. The results of the test showed no noticeable difference in reflectance between the samples. This suggests that the temperature depression and the force of the CO_2 snow cleaning did not have an effect on the physical structure of the polymer matrix (fig. 9).

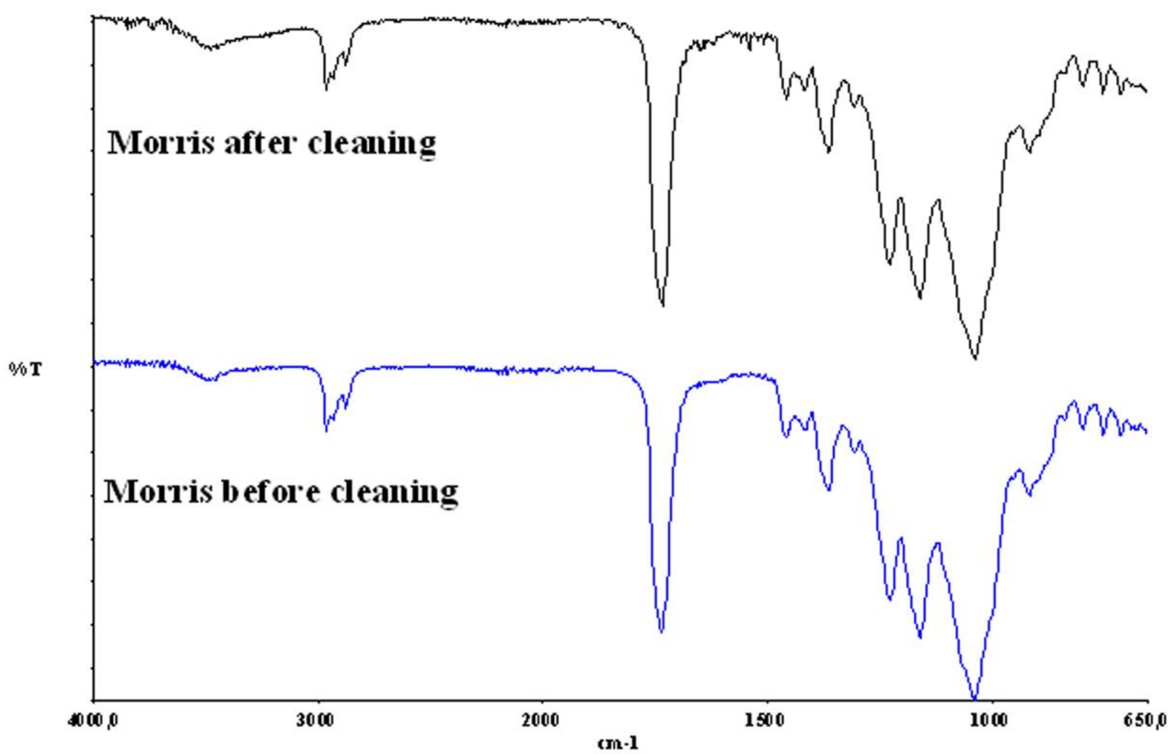

Fig. 9. Spectra produced from the ATR analysis conducted by Yvonne Shashoua

3. MOVING FORWARD WITH CO_2 SNOW

Carbon dioxide snow is a cleaning tool for the conservator's toolbox with its greatest potential yet to be realized. Bench-top anecdotal experimentation suggests that it may be a viable cleaning alternative on a diverse number of materials and object types. Like any tool, it cannot solve all problems and the choice to use the method must be carefully considered. If the general parameters of successful use are observed, CO_2 snow could prove to be a useful cleaning solution for a wide variety of materials. The most important of these parameters to observe are: the soiling type should be particulate or light-hydrocarbon in nature; the surface to be cleaned should be minimally energy absorptive; and the object to be cleaned should not be detrimentally affected by the momentary temperature depression or force produced by the CO_2 jet. Identification of the potential combinations of soiling type and material to be cleaned in the field of conservation has only just begun. The sharing of knowledge from continued experimentation and use of the system will help to facilitate the conservator's understanding of CO_2 snow's effective application to cultural materials.

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NOTE

1. Testing was done in the SAAM Object Conservation Lab in cooperation with Anthony Dessasso, Engineer, of the Smithsonian's OFEO (Office of Facilities Engineering & Operations), custodians of the FLIR imaging unit.

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Sherman, R. 2007. Carbon dioxide snow cleaning. *Particulate Science and Technology* 25(1): 37–57.

FURTHER READING

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SOURCES OF MATERIALS

Nitrogen gas and CO_2 snow unit with gas or liquid CO_2 feed
Applied Surface Technologies
15 Hawthorne Drive
New Providence, NJ 07974

CO_2 snow unit with liquid CO_2 feed
Va-Tran Systems Incorporated
677 Anita St, Suite A
Chula Vista, CA 91911

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