Nevena Krstulović
Ana Bielen
Domagoj Mudronja
Ivana Babić
Nikša Krstulović

The *PlasmaArt* Project – Application of Atmospheric-Pressure Plasma Jets in Conservation-Restoration of Wooden Objects

Nevena Krstulović
Croatian Conservation Institute
Rijeka Department for Conservation
nkrstulovic@h-r-z.hr

Ana Bielen
Zagreb, Faculty of Food Technology and Biotechnology
Laboratory for Biology and Microbial Genetics
abielen@pbf.hr

Domagoj Mudronja
Croatian Conservation Institute
Natural Science Laboratory
dmudronja@h-r-z.hr

Ivana Babić
Faculty of Science
Department of Biology
ibos254@gmail.com

Nikša Krstulović
Institute of Physics
niksak@ifs.hr

Original scientific paper/
Izvorni znastveni rad
Received/Primljen: 2. 5. 2018.

UDK
7.025.3/.4-035.3]:533.9
DOI
http://dx.doi.org/10.17018/portal.2018.10

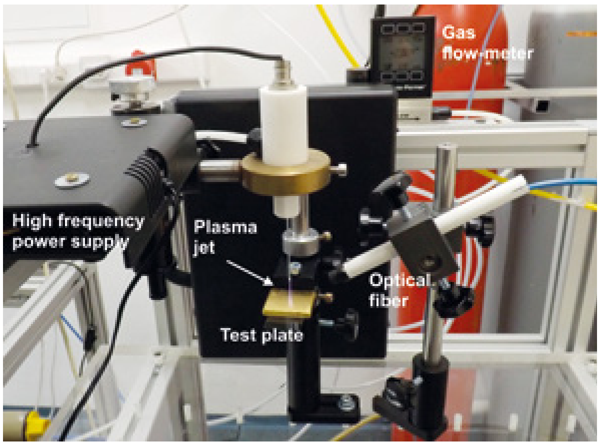
ABSTRACT: The *PlasmaArt* project was realized as a collaboration between the Institute of Physics and the Croatian Conservation Institute. The project was funded mainly by the Funds of the Adris Group, and to a lesser extent by project IP-11-2013-2753 of the Croatian Science Foundation. The main idea of the project was to test the application of cold atmospheric plasma jets on wooden test plates that simulate wooden artwork for the purpose of disinfection and removal of stratigraphic layers of overpaint. For ethical reasons, experimental research was carried out not on real artwork, but on wooden test plates which had been prepared to simulate wooden artefacts. (The samples were silver-plated and gold-plated plates, painted and varnished to faithfully represent real artwork.) To test the efficiency of the disinfection effect, some of the test plates were contaminated with fungal mycelia, and to test the removal of stratigraphic layers, the rest of the silver-plated and gold-plated test plates were covered with several layers of paint and varnish. The prepared test plates were treated with cold atmospheric-pressure plasma jets. The results showed that the stratigraphic layers could not be removed, and it was not possible to remove each layer separately. As a result of the disinfection procedure, positive effects were obtained in comparison to standard procedures used in conservation, while the efficiency depended on the type of plasma and the length of the treatment. It was found that the cold atmospheric-pressure plasma jet was an effective source for disinfection of wooden artwork in the conditions described in this paper.

KEYWORDS: *Conservation-restoration of wooden art, disinfection, wood-rotting fungi, cold atmospheric plasma jet, plasma technology, plasma disinfection, treating material using plasma*

Today's emerging technology based on cold atmospheric pressure is being increasingly used in industrial, medical and technological applications, such as treatment of hard dental tissue, food processing (Plasma Agriculture and Food processing – a new trend in food and seed/grain treatment for enhanced germination, and sterilization of fruits and vegetables using so-called plasma-activated water for enhanced freshness and shelf-life of the products), sterilization of various samples, surface modification, etc. The cold atmospheric plasma jet (or Atmospheric-Pressure Plasma Jet, APPJ) is suitable for the processing of sensitive samples because, on the one hand, it does not cause thermal damage of the sample, and on the other hand it is rich in chemical radicals responsible for the processing of the surfaces. The concentrations of radicals are typically very low (in trace amounts), and radicals are short-lived, so they are not harmful to human health. On the other hand, the concentrations of radicals are sufficient to interact effectively with the treated surface. Furthermore, the plasma jet operates in atmospheric conditions, so there is no need for a vacuum chamber or related equipment, which substantially affects the versatility of application of plasma jets. A plasma-jet device could be compact and portable, which would enable the processing of samples outside the laboratory – *in situ*. Today, various plasma sources for the treatment of artworks are used in conservation/restoration. Below are some examples of previous applications of plasma in restoration/conservation. František Krčma and co-authors[2] used cold, but low-pressure, hydrogen plasma for the removal of corrosion from archaeological metal objects. A problem in heating the material was observed, so the authors conclude that this type of processing is not suitable for wooden objects, as well as for metal objects with surface cracks, due to inhomogeneous distribution of temperature during the processing. Ghiocel Ioanid and co-authors[3] used cold low-pressure plasma for microbial decontamination of polymers. This type of processing deactivated the spores of microorganisms, but did not decompose the polymer, especially not in the deeper layers. Stefano Voltolina and collaborators[4] used a variety of atmospheric commercial plasma sources based on arc or dielectric discharge to clean architectural surfaces such as various types of stone, marble and wall painting. The objects were cleaned of epoxy and acrylic resin and oil paints. It turned out that arc discharges are not suitable for the cleaning of objects due to the problem of deposition of metal on the surface of the samples. Satisfactory results in the cleaning of objects without significant heating of the surface were achieved using dielectric discharge. Anna Comiotto[5] used a miniature source of cold atmospheric plasma to improve the adhesion properties of the plastics that are used in modern and contemporary arts. Promising results of improvement of adhesive properties (binding and coverage) of nonpolar plastic pre-treated with plasma were achived. Christina Pflugfelder and associates[6] used two plasma sources (dielectric discharge and atmospheric plasma jet) to clean wall paintings of resins, varnishes and soot with the process of plasma etching. The results were only partially satisfactory because of the occurrence of unwanted ablation of materials and the different actions of the plasma on different substances. Emil Ioanid and collaborators[7] used low-pressure radio-frequency plasma for decontamination and cleaning of paper supports and for coating paper with polymer protection, and they achieved satisfactory results. Olivier Schalm and colleagues[8] used atmospheric plasma afterglow for removal of sulphite layers from oxidized and pure surfaces of silver and copper. The removal efficiency of the oxide layers depended on their thickness, and it was very difficult to achieve a high gloss on the cleaned samples. K. Schmidt-Ott[9] used low-pressure hydrogen plasma for processing of metallographic samples (iron nails) with the aim of reduction in the corroded layers. Chlorides and sulphides could be fully removed from the surface without damaging the sample. The large collaborative project PANNA[10] (Plasma And Nano for the New Age "soft" conservation) lasted from 2011 to 2014, and it was based on the application of various atmospheric plasma sources for the cleaning of stone, metal and murals of various impurities such as soot, graffiti, corrosion products, oil paints, polymers etc. From this project a new technology of material processing with the use of plasma arose. From the above examples, one can see that the application of various plasma sources in the conservation/restoration of artworks is very broad, but in some cases limited. Thus far, we have not found examples of processing of wooden artwork with atmospheric plasma jets, and this motivated us for the realization of this project called *PlasmaArt*.

The development of the idea of the *PlasmaArt* project

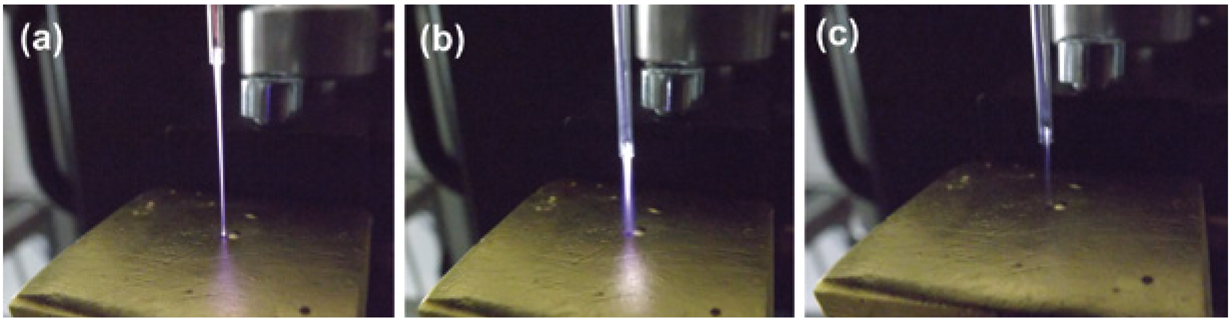
The *PlasmaArt* project was realized as a collaboration between the Institute of Physics, as project developer, and the Croatian Conservation Institute, in cooperation with the Faculty of Food Technology and Biotechnology, and the Department of Biology in the Faculty of Science, of the University of Zagreb[11]. The project was funded mainly by the Funds of the Adris Group, and to a lesser extent by project IP-11-2013-2753 of the Croatian Science Foundation. This project tested the use of cold atmospheric plasma jets on wooden test plates that simulate wooden artwork for the purpose of disinfection and removal of stratigraphic layers of overpaint. For ethical reasons, experimental research was carried out not on real artwork, but on wooden test plates that simulate wooden artwork. The goal of this project is to complement the current practice of disinfection and processing of wooden artwork, which currently uses only standard chemicals and disinfection techniques, with a new technique based on application of atmospheric-pressure plasma jets. It would also develop a completely new concept of treatment that is effective, has the potential of action on site, and may be applied to the treatment of other materials and to other types of cleaning: for example, the removal of graffiti from stone surfaces, which is a great problem and often encountered in restoration/conservation practice, cleaning of stone and marble, cleaning of bronze, silver and gold objects, etc. This project is based on ecologically acceptable plasma technology and fits within the Strategy of protection, preservation and sustainable economic use of the cultural heritage of the Republic of Croatia, as well as with the European policy of protection of cultural heritage[12]. Today, the disinfection/sterilization of artworks made of wood (the destruction of microorganisms on the surface of the wooden artworks) is usually conducted with chemical techniques, such as the use of *Metatin*, *Nipagin*, thymol, cetrimide-based solution, ethanol etc. All of these chemicals are toxic and pose risks to humans and the environment (including the problem of storing waste wadding, and residues on the artwork). During their application it is necessary to use the optimum concentration to avoid, as far as possible, exposure to their harmful effects. Another disadvantage of this technique is that the microbiocidal substance used must be compatible with the relevant materials that are used in the conservation and restoration works on the artworks.[13] Another method of disinfection/sterilization is based on the use of methyl bromide gas. In this method two problems arise: one related to the preservation of health or the environment, and the other associated with outsourcing (i.e. necessarily engaging subcontractors), which makes the process costly and less flexible. Methyl bromide is classified as a severe poison and creates greenhouse gases,[14] and until recently it was used as a pesticide, but has been discontinued and replaced by alternative, less harmful agents. Short-term exposure to high concentrations, or frequent exposure to small concentrations, of this gas is very harmful to humans and causes serious problems with the kidneys and the respiratory and nervous systems. The other method of disinfection/sterilization is based on the use of sulphur gas, which is actually not suitable because it causes the tanning of pigments such as lead whitener.[15] As an alternative to gas-based disinfection there are other ways of treating artworks, but they are in many cases inadequate and harder to execute. For example, the processing of artwork with the help of γ-radiation is often performed in the preservation of cultural heritage,[16] however that treatment has many negative aspects: disinfection cannot be performed *in situ*; the dimensions of the chamber, and thus of the artworks that can be treated, are very limited; the process is very expensive financially; the radiation is radioactive.[17] Today, artworks are often treated with nitrogen gas, which requires that the artwork be delivered to the chamber too, which is expensive and limited by the dimensions of the chamber, and the treatment does not take place *in situ*. In recent conservation and restoration practices, atmospheric impurities, microorganisms and subsequent interventions/copy on layer-painted artworks have been removed by mechanical or chemical means (chemical solvents), which always creates the risk of micro-damage to the surface due to mechanical rubbing or soaking. We have tried to respond to many of these issues and challenges with cold atmospheric-pressure plasma jet.



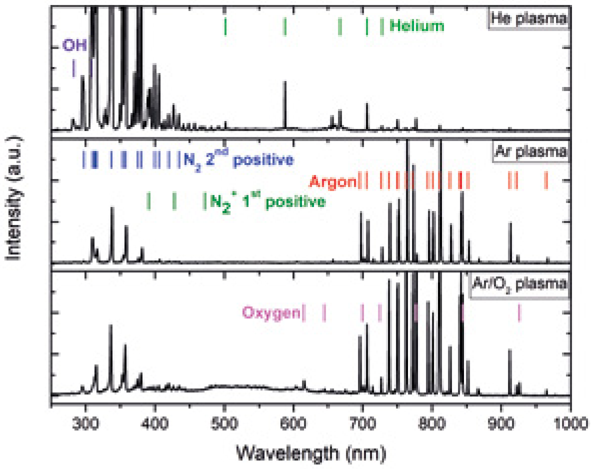
1 Zagreb, PlasmaArt project, experimental collection for treating wooden artwork with atmospheric-pressure plasma jets (Institute of Physics Photo Archive, N. Krstulović, 2017)
Zagreb, projekt PlasmaArt, eksperimantalni postav za obradu drvenih umjetnina pomoću atmosferskog plazmenog mlaza (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)

Principle of operation of atmospheric-pressure plasma jet

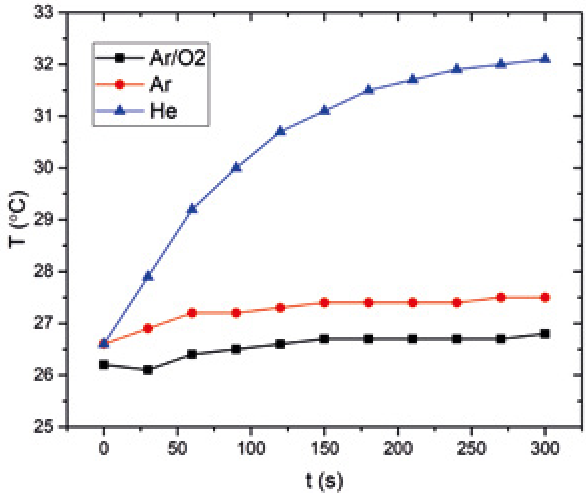
An atmospheric-pressure plasma jet[18] is formed when a gas (Ar, He, or a mixture of Ar and O_2) flows through a glass capillary tube in which an electrode is located. High-frequency (20 kHz) high voltage (7 kV) is applied to the electrode. The experimental set-up of atmospheric-pressure plasma jet for the processing of artwork is shown in **Figure 1**. In **Figure 2**, photos are shown of plasma jets of (a) He, (b) Ar and (c) Ar/O_2 mixture during processing of the gold-plated test plates. One can see that the plasma jets are of different colour, intensity and length. Atmospheric-pressure plasma jets are a type of cold plasma: the jet temperatures are around 30–50 °C, while the heating of the treated materials is much less (just a few °C local increase in the temperature of the treated sample), so there is no thermal damage. What makes this type of plasma



2 Photographs of plasma jets (a) He, (b) Ar and (c) Ar/O_2 mixture (Institute of Physics Photo Archive, N. Krstulović, 2017)
Fotografije plazmenih mlazeva (a) He, (b) Ar i (c) mješavine Ar/O_2 (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)



3 Graphical representation of optical emission of He, Ar and Ar/O_2 plasma-jet spectra with identified atomic, ionic and molecular lines (Institute of Physics Photo Archive, N. Krstulović, 2017)
Grafički prikaz optičkih emisijskih spektara He, Ar i Ar/O_2 plazmenog mlaza sa identificiranim atomskim, ionskim i molekularnim linijama (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)



4 Graphical representation of the heating temperature of a gold-plated test plate treated with He (blue line), Ar (red line) and Ar/O_2 (black line) plasma jet, depending on length of treatment (Institute of Physics Photo Archive, N. Krstulović, 2017)
Grafički prikaz temperature zagrijavanja pozlaćene test-pločice pri obradi He (plava linija), Ar (crvena linija) i Ar/O_2 (crna linija) plazmenim mlazom u ovisnosti o vremenu obrade (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)

chemically reactive is the creation of radicals (OH, O_3, H_2O_2 etc.) and UV light, in the plasma jet and in the area around the jet, which are responsible for the actual processing of the samples (etching, chemical reactions, change of surface properties, sterilization, removal of material from the surface, deactivation of microorganisms, etc.). Processing of samples with plasma jet is contactless (there is no mechanical contact and therefore no mechanical damage), while the distance of the plasma jet from the sample can affect the strength of the interaction with the surface, which can control the efficiency of the processing itself. The idea is that the plasma jet removes impurities from the surface (with the processes of etching by means of oxygen radicals) and deactivates microorganisms like fungi and moulds (UV light, radicals, ozone, peroxide). We also tried to use plasma jet for removal of stratigraphic layers and overpaints. Generally, the plasma jet could replace, to a greater extent, the standard methods that use solvents, alcohols, or methyl bromide. In order to analyse the content of atmospheric-pressure plasma jet (as a free jet or as a jet in contact with the surface of the test plates during processing), optical emission spectroscopy was used. This technique appeared to be a versatile technique not only for the analysis of plasma content, but also for monitoring the interaction processes of the plasma with a variety of samples and for detecting products of the interactions that were in energetically excited states. For example, when processing a surface with low-pressure plasma (there being no dominant influence of nitrogen from the air) it is possible to monitor various processes of interaction between plasma and materials by using optical emission spectroscopy as shown during cleaning of aluminium titanate,[19] treatment of PET foils,[20] modification of ink-jet paper,[21] degradation of bacteria,[22] functionalization of poly(p-phenylene-sulphide),[23] interaction of plasma with aluminium substrates,[24] oxidation of aluminium,[25] detection of water-vapour plasma[26] and time-resolved characterization of the deposition and cleaning of CH films.[27] In Figure 3, the optical emission spectra of He, Ar and Ar/O_2 plasma jets during processing of test plates is shown. (A description of the making of test plates is given in the next chapter.) These spectra correspond to the emission of plasma jets as shown in Figure 2. From the spectra, the atomic emission lines are identified of not only the respective gas emissions, but also the neutral and ionized nitrogen molecules and molecules of OH groups that are ionised and electronically excited due to interaction with the plasma jet. It can be seen that He plasma jet is richest in ultraviolet radiation, while radiation from the Ar and Ar/O_2 plasma is dominant in the near-infrared optical spectrum. It is assumed that the plasma jet interacts with the fungi by etching dominated by ions and atoms of oxygen, as well as chemically through reactions with various beam radicals (peroxide, ozone, NO_x, etc.). Products of etching and chemical reactions cannot be observed in the optical emission spectrum because they are not in energetically excited states, which would lead to the emission of photons and thus allow detection with optical emission spectroscopy. This is expected, because plasma jet is a cold, low-energy plasma type, so the dominant mechanism of action is 'cold etching' without high-energy by-products, which ensures the processing of thermo-sensitive materials without thermal damage. In Figure 4, the surface temperature of the test plates in dependence on treatment time with all three jets of plasma is shown. In this case, the plasma jet was directed at the middle of the test plates, which were fixed (not moved relative to the jet, unlike in treatment of the fungi). It can be seen that the heating is greater when using He plasma, and there is a rise of about 6 °C over the five minutes of treatment, while for the other two plasma types the temperature increase is small, and the amount of increase after 5 minutes is about 1 °C. This heating effect is interesting because, on the basis of emission spectra, it is expected that the test plates will be least heated using a He plasma jet because there the dominant radiation is UV, unlike in the two other sources, where IR radiation prevails. However, heating (although very little) evidently comes from the kind and intensity of interaction between plasma jet and test plate, and this leads us to the conclusion that a plasma jet provides 'cold' but chemically very active sample treatments. We assume that, in our case, the surface of the test plates during the 5 minutes of treatment of fungi increases by less than 1 °C, since the test plates are moved with respect to the plasma jet.

Preparation of wooden test plates

The first step in the realization of the project was the production of wooden test plates that simulate real wood polychromed and gilded artwork. These test plates are shown in Figure 5. For the investigation of the removal of stratigraphic layers by plasma jet, 12 silver-plated and 12 gold-plated tiles (dimensions 3 cm x 3 cm x 2 cm) were fabricated. Metallization was done only on the top surface of the test plates. The test plates were additionally multiply painted and/or varnished in order to more accurately imitate the multiple prints, varnishes and subsequent interventions often found on the real artwork. On the first group of test plates, silver-plated and numbered S1 to S12, the following additional coatings were applied on the surface:
S1 – without further coatings,
S2 – rabbit glue,
S3 – varnish, dammar resin in rectified turpentine,
S4 – varnish, mastic in *Shellsol A*,
S5 – imitation of atmospheric impurities (dust mixed with *Tylose MH 300*),
S6 – 1st layer of stain (dammar varnish + cadmium yellow *MAIMERI® Mastic Retouching Color*), 2nd layer of imitation of atmospheric impurities,
S7 – 1st layer of stain (dammar varnish + ultramarine blue *MAIMERI® Mastic Retouching Color*), 2nd layer of tempera overpaint (viridian + rabbit-skin glue),
S8 – shellac orange,
S9 – 1st layer of shellac orange, 2nd layer of tempera overpaint (scarlet red + rabbit-skin glue), 3rd layer of imitation of atmospheric impurities,
S10 – 1st layer of shellac orange, 2nd layer of tempera overpaint (titanium white + rabbit-skin glue), 3rd layer of mastic resin in *Shellsol A*, 4th layer of imitation of atmospheric impurities,
S11 – 1st layer of stain (carmine red MAIMERI® Mastic Retouching Color + varnish dammar resin in rectified turpentine), 2nd layer of tempera overpaint (ultramarine blue + rabbit-skin glue), 3rd layer of tempera overpaint (sienna brown + rabbit-skin glue), 4th layer of mastic varnish in *Shellsol A*,
S12 – acrylic colour (golden acrylic quinacridone crimson purpurote).
On the second group of test plates, gold-plated and numbered Z1 to Z12, the following additional coatings were applied on the surface:
Z1 – no additional coatings,
Z2 – rabbit-skin glue,
Z3 – varnish, dammar resin in rectified turpentine,
Z4 – varnish, mastic resin in *Shellsol A*,
Z5 – layer of imitation of atmospheric impurities,
Z6 – layer of tempera overpaint (scarlet red + rabbit-skin glue),
Z7 – 1st layer of dammar varnish in rectified turpentine, 2nd layer of imitation of atmospheric impurities,
Z8 – 1st layer of tempera overpaint (viridian + rabbit-skin glue), 2nd layer of varnish, mastic resin in *Shellsol A*,
Z9 – 1st layer of rabbit-skin glue, 2nd layer of tempera overpaint (orange + rabbit-skin glue), 3rd layer of dammar varnish in rectified turpentine, 4th layer of imitation of atmospheric impurities,
Z10 – bitumen,
Z11 – 1st layer bitumen, 2nd layer of imitation of atmospheric impurities,
Z12 – acrylic paint (golden acrylic quinacridone crimson purpurote).

In the second part of the project, the efficiency of a cold plasma jet for disinfection of wooden test plates was tested. Therefore, gold-plated test plates of three different types of wood (linden, spruce, beech) were made, because most of the wooden polychromed sculptures in our area are made of that particular wood. For the main test, the test plates were made only of linden wood; they were then contaminated with fungal mycelium and then treated with an atmospheric plasma jet.

Cultivation of wood-rotting fungi on wooden test plates

Wood-rotting fungi from the Basidiomycota group often cause the biological degradation of woodwork, especially in combination with insects.[28] The rotting often develops in churches and other historical buildings on wooden statues, altars, roof constructions etc.[29] The fungi grow in the form of three-dimensional mycelium (i.e. a mass of branched hyphae) that penetrates deep into the wood (substrate) but also develops above the surface (i.e. aerial

5 Wooden test plates as a simulation of real polychrome and gold-plated artwork (Croatian Conservation Institute Photo Archive, G. Tomljenović, 2017)
Drvene testne pločice kao simulacija prave polikromirane i pozlaćene umjetnine (fototeka HRZ-a, snimio G. Tomljenović, 2017.)

mycelium). During their growth, the hyphae secrete extracellular enzymes that break down cellulose to glucose. Due to the depth of penetration, it is difficult to mechanically remove the fungi from the surface, and chemical treatment is often ineffective. Furthermore, fungi contaminate their surroundings by discharging numerous microscopic exospores into the environment. The spores are transmitted by air, are highly resistant to unfavourable conditions, and can germinate after very long periods. If the conditions are favourable, as is often the case in poorly ventilated, humid areas, spores germinate into a new mycelium on a suitable substrate. To investigate the effect of cold atmospheric plasma jet on the test plates contaminated with model wood-rotting fungal species, in the first phase of the project we modified the existing EN 113 method[30] in order to achieve good fungal growth on the simulated wooden artefacts (test plates). We compared the growth dynamics of two common wood-rotting fungal species: *Serpula lacrymans* (CBS 235.33) and *Coniophora puteana* (CBS 117468). We also compared the growth of the fungi on test plates made of various types of wood: spruce, linden and beech (dimensions 3 cm x 3 cm x 2 cm). On the upper side of the test plates a chalk layer was applied, with a red coating-bolus and gold leaf on top, while the other sides of the test plates were without any coating (bare wood). All the plates were sterilized by γ-radiation (dose 25 kGy)[31] before the fungal infection, in order to exclude the possibility of contamination with other undesirable microorganisms. Some of the test plates were weighed, dried at 103 °C, and then weighed again in order to calculate a moisture content of about 8 %. The fungi were grown on wooden test plates in lidded glasses (volume 500 mL), as shown in **Figure 6**. Besides the test plate, placed on a cylindrical stand, the glasses also contained vermiculite soaked with an appropriate liquid growth medium. The vermiculite maintains the high degree of moisture in the system necessary for fungal growth. The glasses, with the vermiculite, were sterilized (121 °C, 210 kPa, 30 min) before the addition of the fungi and γ-radiated test plates. Before the experiments, the fungi were grown on appropriate solid media: *C. puteana* on malt agar and *S. lacrymans* on malt yeast extract agar (YM agar). Pieces of agar grown with mycelia (5 mm x 5 mm) were placed on the test plates in several different ways in order to determine which plate-inoculation method was most successful:

A – the gold-plated side up and the fungi on top of it: simulation of actual conditions of art infestation,

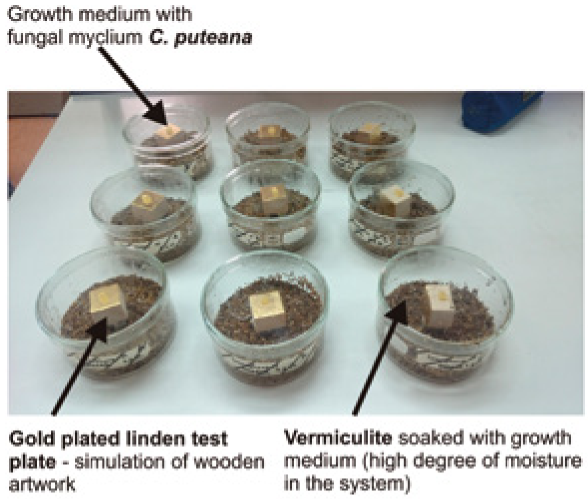
B – the gold-plated side up, deliberately scratched with a razor, and the fungi on top of it: simulation of damaged wooden artefact, and

C – the bare-wood side up and the fungi on top of it.

The fungal growth was monitored for 30 days at 18 °C with a relative humidity of 65 ± 5 %. The results showed that *C. puteana* grew faster than *S. lacrymans*, although both species grew across the entire top of the test plate after two weeks and then spread to its lateral surfaces. Furthermore, both species grew successfully on test plates made of all three types of wood. Likewise, the mode of test-plate inoculation (A, B or C) did not affect the fungal growth rate, which shows that the coating of the test plates (chalk backing, bolus, gold leaf) was not an obstacle to the penetration of the mycelium. At the end of this preliminary experiment, it was found that in all cases the fungi spread through the coating, damaged it and abundantly contaminated the wood, even when the mycelium was applied directly to the undamaged coating (A). On the basis of these results, the testing of the effects of cold atmospheric plasma jets on the test plates contaminated with fungi was carried out only with the fast-growing *C. puteana* species, which was placed directly on the undamaged upper gold-coated surface of the linden test plates.

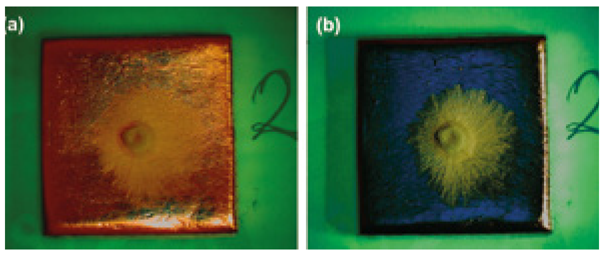
Analysis of the effects of cold atmospheric plasma jets on *C. puteana* fungus grown on gold-plated wooden test plates

In this study, we have investigated the potential of cold atmospheric plasma jets for the disinfection of wooden artefacts contaminated by wood-rotting fungi, using *C. puteana* as a model organism and the modified EN 113 method as a test system. Briefly, *C. puteana* was applied to the gold-coated surface of the test plate and grown for 7 days at 18 °C or until the mycelium had sufficiently grown (covering a certain percentage of the upper gold-coated surface of the test plates). Subsequently, the samples were treated with different types of atmospheric cold plasma jets (day 0, gases He, Ar and Ar/O_2) and the results were compared with traditional disinfection methods. After treatment, the samples were returned to the system to monitor the recovery of the fungi after 5 and 8 days. In order to study the effectiveness of the disinfection of those test plates contaminated with *C. puteana* by atmospheric cold plasma jet, treatments were performed with three different gases (helium, argon and a mixture of argon (90 %) and oxygen (10 %)) and two processing times (2 and 5 minutes). For comparison, the test plates were treated with ethanol and also mechanically (standard cleaning in restoration/conservation). Each treatment was performed on 3 test plates to allow for statistical analysis of the results. Treatments were done in the vicinity of a Bunsen burner, to ensure sterile laboratory conditions. During the treatments, the plasma jet was at a distance of 1.5 cm from the surface of the sample in the case of He, and 1 cm in the cases of Ar and Ar/O_2 mixture. The sample was moved in relation to the plasma jet in order to be uniformly treated with plasma. Thus, the entire upper surface contaminated with the fungi was exposed to plasma jet, and this procedure was repeated several times depending on the length of the treatment. Measurements of the test-plate area covered by fungal mycelium were taken at 3 different time points.

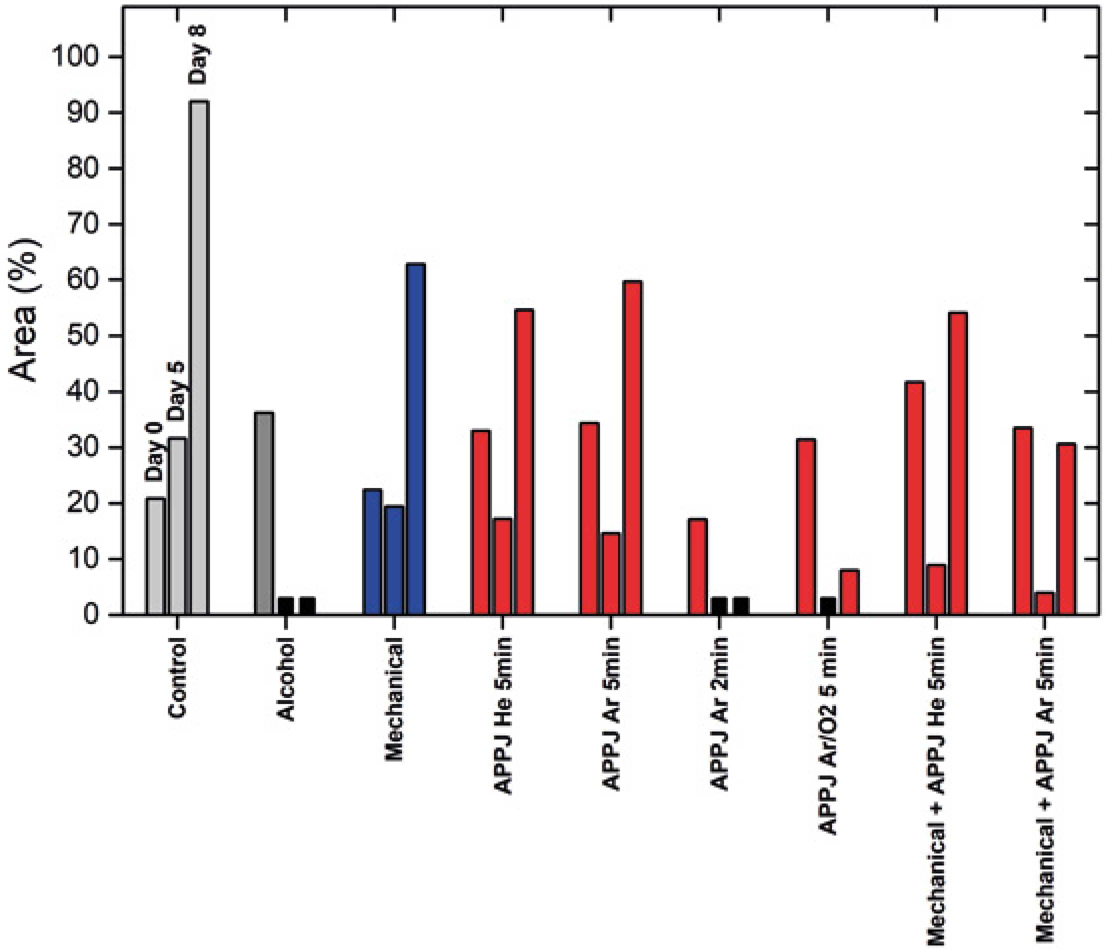


6 System for cultivating wood-rotting fungi *Serpula lacrymans* and *Coniophora puteana* on test plates (Faculty of Food Technology and Biotechnology Photo Archive, D. Šikić, 2017)
Prikaz sustava za uzgoj gljivica na testnim pločicama (fototeka Prehrambeno-biotehnološkog fakulteta, snimila D. Šikić, 2017.)

The measurements were first taken immediately before treatment (day 0), the second time 5 days after the treatment (day 5), and the third time 8 days after the treatment (day 8). The images were captured with a Dino-Lite USB microscope in visible and ultraviolet light, and processed using the ImageJ program to determine the area covered by fungal mycelium. **Figure 7** shows the test plates contaminated with *C. puteana* type photographed under (a) visible and (b) UV light. The surface area of the test plate covered by fungal mycelium, used for quantization, can be seen clearly under UV light. **Figure 8** shows the area covered by fungal mycelium before and after plasma treatment, as well as the control samples – an untreated sample, a sample treated with 96 % ethanol, and a sample where the fungi were mechanically removed with wool (also in the standard way used in restoration/conservation practice). Instead of



7 Macrophotographs of test plates infected with *C. puteana* taken with a microscope under (a) visible and (b) UV light: Under UV light, the edge of the surface area of the test plate covered with the fungi is clearly visible (Institute of Physics Photo Archive; N. Krstulović, 2017)
Makrofotografije testne pločice inficirane vrstom C. puteana snimljene mikroskopom pod (a) vidljivim i (b) UV svjetlom. Pod UV svjetlom jasno se vidi granica zahvaćenosti površine testne pločice gljivicom (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)



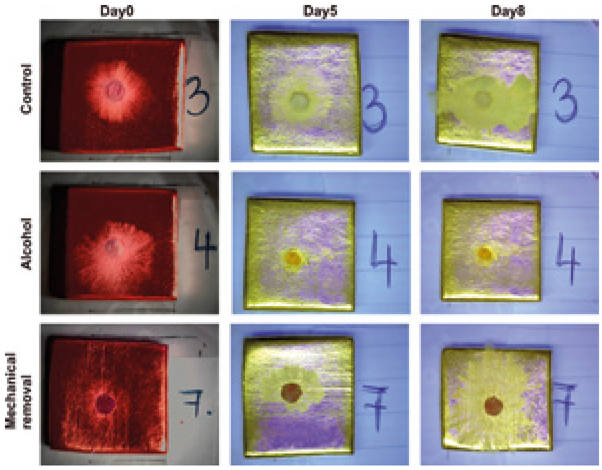
8 Graphical representation of the test plate's surface coverage before (day 0) and after (day 5 and day 8) treatment with He, Ar and Ar/O_2 plasma jet. Black squares mean there is no growth of microorganisms.

Grafički prikaz površine pokrivenosti testne pločice prije (dan 0) i poslije (dan 5 i dan 8) obrade s He, Ar i Ar/O_2 plazmenim mlazom. Crni kvadratići znače da nema napredovanja širenja mikroorganizama.

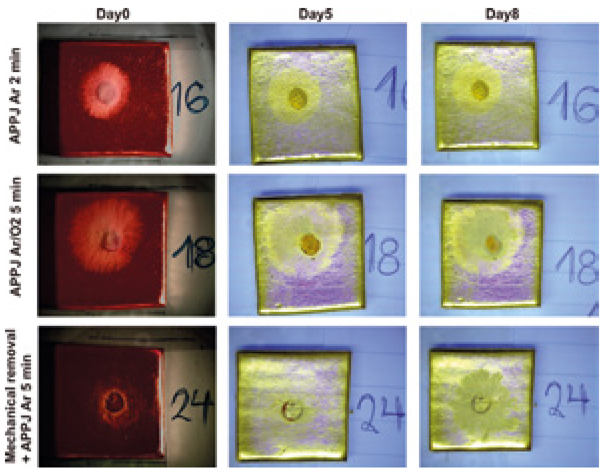
standard 70 %, the 96 % ethanol was used because of the test plate surface high sensitivity to water. Other samples were treated with different types of plasma jets, and for two different processing times. In the untreated control sample, fungal coverage increased about four- to five-fold in 8 days. Moreover, after the 8th day, the mycelium began also to cover the side panels of the test plate and grow in height. This rapid fungal growth observed in negative control was reduced or completely stopped by treatment with ethanol (positive control) and plasma jet. In the figure, black squares denote samples with no growth after the treatment, and two consecutive black squares indicate that the fungi were completely deactivated. Thus, ethanol treatment was lethal for the fungi, since after processing there was no further mycelial growth. However, ethanol treatment visibly damaged the coating of the test plate. On the other hand, after mechanical cleaning of the samples, the fungi progressed, and after 8 days even grew over the lateral surfaces of the test plate. All plasma treatments caused a reduction in the surface covered with mycelium measured after 5 days; in some cases, more than 90 % of the initial mycelium-covered surface (treatments that involved a mechanical-removal step, followed by treatment with Ar and He plasma jets). Moreover, in some cases the mycelium completely disappeared from the surface of the test plate (Ar and Ar/O_2 plasma). Figure 9 shows photographs of the fungal progression in the negative control sample, as well as in the samples cleaned mechanically or with ethanol. On the sample cleaned with ethanol, macroscopic damage of the gold coating is clearly visible. It is also visible that there was no further growth of the mycelium after processing. On the mechanically cleaned sample, it can be seen that the fungi have grown outside the upper test-plate surface after 8 days. Figure 10 shows photos of fungal growth for samples treated with Ar and Ar/O_2 plasma jets (processing length 2 and 5 minutes), and for a sample which was first mechanically cleaned and then treated with Ar plasma jet for 5 minutes. After treatment of the sample with Ar plasma there was no further mycelial growth, and the gold coating on the surface of the test plate was not damaged as it was in the case of ethanol treatment. After the treatment, the mycelium simply degraded at the surface of the test-plate, and the plate was clear and fungus-free, showing matte morphology in the area previously covered in mycelium. It should be emphasized that this result is the best example of the efficiency of a plasma-jet treatment. After treatment with the Ar/O_2 plasma jet, mycelial growth first completely stopped (no mycelium found on the test-plate surface 5 days after treatment), and then somewhat re-appeared (after 8 days). The combination treatment (mechanical cleaning followed by plasma-jet treatment) had a favourable effect, since after 5 days the results were much better than the mechanical removal of the fungi alone. Mycelium coverage after 8 days was roughly the same as initial, which is certainly better than 8 days after the mechanical treatment alone (much larger surface covered by mycelium). Finally, in this kind of plasma-jet treatment we observed a problem of exposure of fungi to the plasma jet. Namely, hyphae that penetrate deeper into the wood, or under the gold coating, showed the ability to survive the plasma-jet treatment and subsequently re-appear on the surface. In order to gain better insight into this problem, additional research is needed. In conclusion, the application of cold atmospheric plasma jet in the treatment of test plates contaminated with fungi has shown a positive effect, i.e. a reduction in growth rate or even complete removal of fungi from the plate. Compared to the control sample, in which mycelial growth was rapid, the effect is obvious. The use of plasma jet is also much more effective than mechanical removal of fungi. Further, in some cases plasma treatments showed results comparable with ethanol cleaning, but plasma did not damage the coating (while the ethanol treatment did), which is certainly an advantage.

Results and analysis of micro-cross-sections of test plates after testing the possibility of removal of stratigraphic layers

Treatment of test plates for testing the efficiency of removal of the stratigraphic layers with the plasma jet was performed in such a way that the jet was either directed at a single point on the surface of the test plate, or the test plate was scanned by the jet. Treatment times varied, and Ar and He plasma jets were used to get positive visual changes on the surface of the gold-plated and silver-plated test plates with additional layers of paint, varnish and simulations of atmospheric impurities.[32] The plasma jet (capillary-tube orifice) was placed at a distance of 0.5 cm from the test plate's surface during treatments. Figure 11 illustrates treatment of different copies using He plasma jet. Micro-specimens of the test-plate layer were taken before and after treatment in order to assess the efficiency of removing the stratigraphic layers. The samples were then immersed in a polyester resin, and after curing they were crushed and polished. From such samples micro-cross-sections were taken and photographed by an

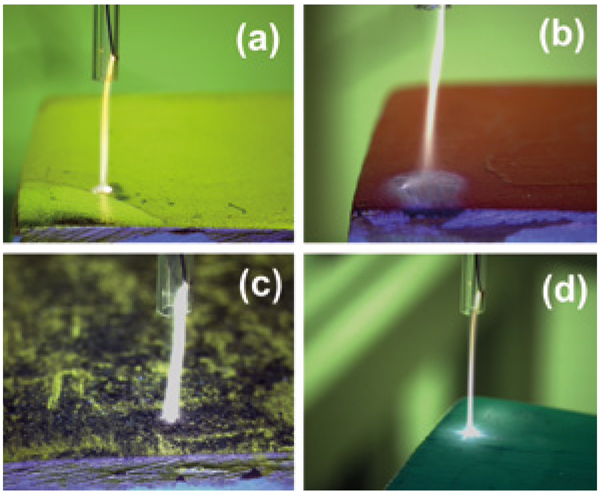


9 Macrophotographs of test plates before (day 0) and after (day 5 and day 8) alcohol treatment and mechanical removal of microorganisms. The first row is a control sample (Institute of Physics Photo Archive, N. Krstulović, 2017)
Makrofotografije testnih pločica prije (dan 0) i poslije (dan 5 i dan 8) obrade alkoholom i mehaničkim odstranjivanjem mikroorganizama. Prvi red predstavlja kontrolni uzorak (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)

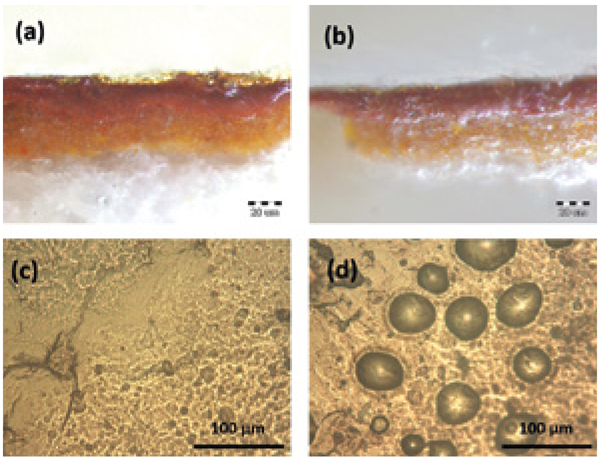


10 Macrophotographs of test plates before (day 0) and after (day 5 and day 8) treatment with Ar and Ar/O_2 plasma jet (first and second row), as well as a combination of mechanical removal and treatment with the Ar plasma jet (last row) (Institute of Physics Photo Archive, N. Krstulović, 2017)
Makrofotografije testnih pločica prije (dan 0) i poslije (dan 5 i dan 8) obrade Ar i Ar/O_2 plazmenim mlazom (prvi i drugi red) te kombinacijom mehaničkog uklanjanja i obrade s Ar plazmenim mlazom (zadnji red) (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)

Olympus DP71 digital camera on an Olympus BX 51 microscope with reflective light and reflected fluorescent light at 365–395 nm; emission at 397 nm. It was observed that the surface of a silver sheet oxidizes in contact with a plasma jet if there is no protective layer (e.g. varnish) on the surface. It was concluded that this type of plasma cannot remove the stratigraphic layer from the surface, but a



11 Removing layers of overpaint using He plasma jet on (a) gold-plated test plate coated with mastic varnish (sample Z2), (b) gold-plated test plate with red tempera overpaint (sample Z6), (c) gold-plated test plate with imitation of atmospheric impurities (sample Z5) and (d) gold-plated test plate with green tempera overpaint and varnish (sample Z8).
Uklanjanje preslika pomoću obrade plazmenim mlazom He sa: (a) pozlaćene testne pločice premazane mastiks lakom (uzorak Z2), (b) pozlaćene testne pločice s crvenim tempernim preslikom (uzorak Z6), (c) pozlaćene testne pločice s imitacijom atmosferske nečistoće (uzorak Z5) i (d) pozlaćene testne pločice s zelenim tempernim preslikom i lakom (uzorak Z8)



12 Microphotographs of cross sections of samples of the painted layer from gold-plated test plates with mastic varnish (a) before and (b) after treatment with plasma jet (Croatian Conservation Institute photo archive; D. Mudronja, 2017); Microscopic image of the test plate's surface with a layer of mastic varnish (c) before and (d) after the plasma jet treatment (Institute of Physics Photo Archive, N. Krstulović, 2017)
Mikrofotografije poprečnih presjeka uzoraka slikanog sloja pozlaćenih testnih pločica s mastiks lakom (a) prije i (b) nakon tretmana plazmenim mlazom (fototeka HRZ-a, snimio D. Mudronja, 2017.); Mikroskopska slika površine testnih pločice sa slojem mastiks laka (c) prije i (d) nakon tretmana plazmenim mlazom (fototeka Instituta za fiziku, snimio N. Krstulović, 2017.)

noticeable morphological change in the treated layer was observed. The characteristic results are shown in Figure 12, showing a micro-cross-section of a sample of a gold-plated test plate with a mastic varnish layer before (a) and after (b) plasma-jet treatment. The varnish layer is present at the test plate surface after processing. Also in Figure 12, a microscopic image of the surface before (c) and after (d) treatment of a gilded test-plate with a mastic varnish layer is shown, in which the varnish layer's morphological structure is changed after treatment. It can visually be observed that the varnish surface become matured after treatment. The morphological changes in the varnish layers formed after plasma-jet treatment demand further investigation in terms of chemical changes and possibly increased hydrophobicity (increased contact angle), i.e. improving the resistance of varnish to moisture.[33]

Conclusion

Cold atmospheric-pressure plasma jet is a new and unexplored source for treatment of wooden objects for applications in restoration/conservation of artworks. The *PlasmaArt* project is the first project where plasma jet has been used for treatment of organic materials such as wood. It was found that plasma jet cannot be used for removal of stratigraphic layers, especially not for removal layer by layer. When silver-plated test plates are treated with plasma jet, an oxide layer is formed on the surface of the plate if there is no protective coating (such as varnish). However, morphological change in treated surfaces is evident, especially in those which possess a varnish coating, such as samples S3, S4, Z3 and Z4. Morphological changes may reduce or increase hydrophilicity or hydrophobicity, which is an interesting topic for further research. The main goal of the project is to test the disinfection of wooden artwork using various types of plasma jet. It was shown that plasma jet significantly reduces the growth rate of fungi, or completely removes them from the test plates. Results of disinfection and removal of fungi are comparable to, or even better than, those obtained by standard methods such as ethanol cleaning or mechanical removal. The other advantage of using plasma jet is that the gold-plated surface is not damaged at all after treatment, whereas it is with the above-mentioned standard techniques. The *PlasmaArt* project has opened a new frontier in conservation/restoration practices for the treatment, by plasma jet, of thermo-sensitive materials such as not only wood, but also paper and canvas. This will be a topic of our further interdisciplinary research.

Acknowledgments

We acknowledge the Adris Foundation for the main financial support of the *PlasmaArt* project. Our thanks also go to project IP-11-2013-2753 of the Croatian Science Foundation for usage of experimental equipment. ■

Notes

1 MOUNIR LAROUSSI, 2002, 1409–1415.
2 FRANTIŠEK KRČMA et al., 2014, 1–10.
3 GHIOCEL IOANID, AURELIA IOANID, DORINA PAEPAUTA, 2007, 441–447.
4 STEFANO VOLTOLINA et al., 2014, 1–3.
5 ANNA COMIOTTO, 2009, 25–35.
6 CHRISTINA PFLUGFELDER, NILS MAINUSCH, IVO HAMMER, WOLFGANG VIÖL, 2007, S516–S521.
7 EMIL G. IOANID, VIORICA FRUNZĂ, DORINA RUSU, ANA MARIA VLAD, CATALIN TANASE, SIMONA DUNCA, 2015, 760–764.
8 OLIVIER SCHALM, 2018, 32–42.
9 KATHARINA SCHMIDT-OTT, 2004, 235–246.
10 ALESSANDRO PATELLI, Plasma And Nano for New Age "soft" conservation, Collaborative project, https://cordis.europa.eu/project/rcn/101319_en.html
11 11 The plasma-jet device was developed at the Institute of Physics, where the treatment of samples was also performed. In the Croatian Restoration Institute's Restoration Department of Rijeka, the wooden test plates were fabricated, while in the Natural Science Laboratory the micro-cross-sections before and after the plasma-jet treatment were analysed. At the Faculty of Food Technology and Biotechnology, University of Zagreb, the cultures of fungi were grown on the wooden test plates, and the samples were analysed after treatment.
12 On the web pages of the Ministry of Culture of the Republic of Croatia, it is stated that the mission of the Republic of Croatia is to "protect, preserve and improve the protection of cultural heritage and foster the development of its use in a sustained way". (Strategy of protection, preservation and sustainable economic usage of cultural heritage of the Republic of Croatia for the period 2011–2015). On the web pages of the European Commission (http://ec.europa.eu/culture/policy/culture-policies/cultural-heritage_en.htm) the importance of protection of cultural heritage is emphasized: "The cultural heritage of the European Union is a rich and diverse mosaic of cultural and creative expressions, our inheritance from previous generations of Europeans and our legacy for those to come". This project evidently fits within the Strategy of protection of the cultural heritage of RH. We also believe that it will fit within future related strategies in RH and the EU.
13 Seminar Microbiological destruction of cultural monuments. Book of Abstracts, FELICITA BRIŠKI, Microorganisms on cultural monuments: from sampling and analysis to choice of microbiocide chemicals, Zagreb, 2000, 36–38: 37.
14 FRANCESCA TONINI, 2015, 163–182.
15 Idem., 175.
16 BRANKA KATUŠIN-RAŽEM, MARIO BRAUN, DUŠAN RAŽEM, 2017, 191–196.
17 ACHIM UNGER, ARNO P. SCHNIEWIND, WIBKE UNGER, 2001, 348.
18 MOUNIR LAROUSSI, TAMER AKAN, 2007, 777–788.
19 ALENKA VESEL et al., 2006, 577–584.
20 NIKŠA KRSTULOVIĆ et al., 2006, 3799–3804.
21 ALENKA VESEL et al., 2007, 3689–3696.
22 DANIJELA VUJOŠEVIĆ et al., 2007, 103305.
23 UROŠ CVELBAR et al., 2007, 8669–8673.
24 MIRAN MOZETIČ et al., 2008, 868–869.
25 NIKŠA KRSTULOVIĆ et al., 2009, 245–249.
26 ZLATKO KREGAR et al., 2009, 145201.
27 MARIJAN BIŠĆAN et al., 2010, 401–412.
28 KATJA STERFLINGER, PASCAL QUERNER, 2016, 47–53.
29 MARGARITA KISTERNAYA, VALERY KOZLOV, 2009, 7–10
30 WEI DONGSHENG, OLAF SCHMIDT, WALTER LIESE, 2013, 349–356.
31 Sterilization was processed at the Ruđer Bošković Institute by means of a Panoramic device for radiation positioned at the Laboratory for Radiation Chemistry and Dosimetry. Contact: Branka Mihaljević.
32 NEVENA KRSTULOVIĆ, DOMAGOJ MUDRONJA, NIKŠA KRSTULOVIĆ, 2017, 24.
33 This is assumed because it is known that plasma jet changes morphological and chemical properties of surfaces, changing their hydrophilicity or hydrophobicity.

Literature

MARIJAN BIŠĆAN, ZLATKO KREGAR, NIKŠA KRSTULOVIĆ, SLOBODAN MILOŠEVIĆ, Time-Resolved Spectroscopic Characterization of a-C:H Deposition by Methane and Removal by Oxygen Inductively Coupled RF Plasma, *Plasma Chemistry and Plasma Processes*, 30 (2010), 401–412.

ANNA COMIOTTO, Miniaturized cold atmospheric plasma for improving the adhesion properties of plastics in modern and contemporary art, *AIC Objects Specialty Group Postprints*, 16 (2009), 25–35.

UROŠ CVELBAR, MIRAN MOZETIČ, ITA JUNKAR, ALENKA VESEL, JANEZ KOVAČ, ALEKSANDER DRENIK, TJAŠA VRLINIČ, NINA HAUPTMAN, MARTA KLANJŠEK-GUNDE, BOŠTJAN MARKOLI, NIKŠA KRSTULOVIĆ, SLOBODAN MILOŠEVIĆ, FREDDY GABORIAU, THIERRY BELMONTE, Oxygen plasma functionalization of poly(p-phenilene sulphide), *Applied Surface Science*, 253 (2007), 8669–8673.

WEI DONGSHENG, OLAF SCHMIDT, WALTER LIESE, Method to test fungal degradation of bamboo and wood using vermiculite as reservoir for moisture and nutrients, *Maderas: Ciencia y tecnología*, 15.3 (2013), 349–356.

EMIL G. IOANID, VIORICA FRUNZĂ, DORINA RUSU, ANA MARIA VLAD, CATALIN TANASE, SIMONA DUNCA, Radio-Frequency Plasma Discharge Equipment for Conservation Treatments of Paper Supports, *International Journal of Chemical and Molecular Engineering*, 9 (2015), 760–764.

GHIOCEL IOANID, AURELIA IOANID, DORINA PAEPAUTA, New Tendencies in Restoration-Conservation: The HF Plasma, *Revue Roumaine de Chimie*, 52 (2007), 441–447.

BRANKA KATUŠIN-RAŽEM, MARIO BRAUN, DUŠAN RAŽEM, Massive Preservation of War-Damaged Cultural Heritage Objects in Croatia by Irradiation, *Uses of Ionizing Radiation for Tangible Cultural Heritage Conservation*, (ed.) Sunil Sabharwal, Vienna, 2017, 191–196.

MARGARITA KISTERNAYA, VALERY KOZLOV, Wood science approach for the preservation of historic timber structures, *International Conference on Wooden Cultural Heritage*, (ed.) Uwe Noldt, Hamburg, 2009, 7–10.

FRANTIŠEK KRČMA et al., Application of low temperature plasmas for restoration/conservation of archaeological objects, *Journal of Physics: Conference Series*, 565 (2014), 1–10.

ZLATKO KREGAR, NIKŠA KRSTULOVIĆ, NATAŠA GLAVAN VUKELIĆ, SLOBODAN MILOŠEVIĆ, Space and time resolved optical emission spectroscopy characterization of inductively coupled RF water vapour plasma, *Journal of Physics D: Applied Physics*, 42 (2009), 145201.

NEVENA KRSTULOVIĆ, DOMAGOJ MUDRONJA, NIKŠA KRSTULOVIĆ, Treatment of wooden artifacts with atmospheric pressure plasma jet, *24th International Scientific Meeting on Vacuum Science and Technique*, (eds.) Maja Buljan and Marko Karlušić, Zagreb, 2017, 24.

NIKŠA KRSTULOVIĆ, IRENA LABAZAN, SLOBODAN MILOŠEVIĆ, UROŠ CVELBAR, ALENKA VESEL, MIRAN MOZETIČ, Optical emission spectroscopy characterization of oxygen plasma during treatment of a PET foil, *Journal of Physics D: Applied Physics*, 39 (2006), 3799–3804.

NIKŠA KRSTULOVIĆ, UROŠ CVELBAR, ALENKA VESEL, SLOBODAN MILOŠEVIĆ, MIRAN MOZETIČ, An optical-emission spectroscopy characterization of oxygen plasma during oxidation of aluminium foils, *Materials and technology*, 43 (2009), 245–249.

MOUNIR LAROUSSI, Nonthermal Decontamination of Biological Media by Atmospheric-Pressure Plasmas: Review, Analysis, and Prospects, *IEEE Transactions on Plasma Science*, 30 (2002), 1409–1415.

MOUNIR LAROUSSI, TAMER AKAN, Arc-free atmospheric pressure cold plasma jets: a review, *Plasma Processes and Polymers*, 4 (2007), 777–788.

MIRAN MOZETIČ, UROŠ CVELBAR, ALENKA VESEL, NIKŠA KRSTULOVIĆ, SLOBODAN MILOŠEVIĆ, Interaction of Oxygen Plasma With Aluminium Substrates, IEEE Transaction on Plasma Science, 36 (2008), 868–869.

ALESSANDRO PATELLI, How effective are reducing plasma afterglows at atmospheric pressure in removing sulphide layers: Application on tarnished silver, sterling silver and copper, *Surface and Interface Analysis*, 50 (2018), 32–42.

CHRISTINA PFLUGFELDER, NILS MAINUSCH, IVO HAMMER, WOLFGANG VIÖL, Cleaning of Wall Paintings and Architectural Surfaces by Plasma, *Plasma Processes and Polymers*, 4 (2007), S516–S521.

OLIVIER SCHALM, PATRICK STORME, ARIANNA GAMBIRASI, MONICA FAVARO, KATHARINA SCHMIDT-OTT, Plasma-Reduction: Its Potential for Use in the Conservation of Metals, *Proceedings of Metal*, (2004), 235–246.

KATJA STERFLINGER, PASCAL QUERNER, Fungi and insects as deterioration agents in museums – a comparison, *Integrated Pest Management (IPM) in Museums, Archives and Historic Houses*, (eds.) Pascal Querner, David Pinninger and Astrid Hammer, Vienna, 2016, 47–53.

FRANCESCA TONINI, La scultura lignea tecniche e restauro: manuale per allievi restauratori, *L'Intervento di restauro sul supporto logneo*, (ed.) Daphne De Luca, Saonara, 2015, 163–182.

ACHIM UNGER, ARNO P. SCHNIEWIND, WIBKE UNGER, Conservation of Wood Artifacts, Physical control methods, Berlin, 2001.

ALENKA VESEL, MIRAN MOZETIC, ALEKSANDER DRENIK, SLOBODAN MILOSEVIC, NIKSA KRSTULOVIC, MARIANNE BALAT-PICHELIN, IGOR POBERAJ, DUSAN BABIC, Cleaning of Porous Aluminium Titanate by Oxygen Plasma, *Plasma Chemistry and Plasma Processes*, 26 (2006), 577-584.

ALENKA VESEL, MIRAN MOZETIC, ALES HLADNIK, JOZICA DOLENC, JANJA ZULE, SLOBODAN MILOSEVIC, NIKSA KRSTULOVIC, MARTA KLANJŠEK-GUNDE AND NINA HAUPTMANN, Modification of ink-jet paper by oxygen-plasma treatment, *Journal of Physics D: Applied Physics*, 40 (2007), 3689-3696.

STEFANO VOLTOLINA et al., PANNA Project: Assessment of a novel methodology for plasma cleaning, coating application and diagnostics and coating removal, *VIII Congresso Nazionale di Archeometria Scienze e Beni Culturali: stato dell'arte e prospettive*, Bologna, 2014, 1-3.

DANIJELA VUJOŠEVIĆ, MIRAN MOZETIČ, UROŠ CVELBAR, NIKŠA KRSTULOVIĆ, SLOBODAN MILOŠEVIĆ, Optical emission spectroscopy characterization of oxygen plasma during degradation of Escherichia coli, *Journal of Applied Physics*, 101 (2007), 103305.

Sažetak

Nevena Krstulović, Ana Bielen, Domagoj Mudronja, Ivana Babić, Nikša Krstulović

PROJEKT PLASMAART: PRIMJENA ATMOSFERSKOG PLAZMENOG MLAZA U KONZERVIRANJU-RESTAURIRANJU DRVENIH PREDMETA

Projekt *PlasmaArt* realiziran je kao suradnja Instituta za fiziku (kao nositelja projekta) i Hrvatskog restauratorskog zavoda uz suradnju s Prehrambeno-biotehnološkim fakultetom i Biološkim odsjekom Prirodoslovno-matematičkog fakulteta. Projekt je poglavito financiran sredstvima Zaklade Adris grupe i manjim dijelom projektom IP-11-2013-2753 Hrvatske zaklade za znanost, a njime smo ispitali primjenu hladnog atmosferskog plazmenog mlaza na drvenim testnim pločicama koje vjerno simuliraju umjetnine od drva u svrhu dezinfekcije i uklanjanja stratigrafskih slojeva oslika. Iz etičkih razloga eksperimentalna ispitivanja nisu provedena na pravim umjetninama. Atmosferski plazmeni mlaz nastaje tako da se kroz staklenu kapilaru u kojoj je smještena elektroda propuhuje plin (Ar, He ili mješavina Ar i O_2). Na elektrodu se narine visokofrekventni (20 kHz) visoki napon (7 kV). Atmosferski plazmeni mlazovi hladni su tip plazmi, temperature mlazova su oko 30 - 50 °C, dok je zagrijavanje tretiranog materijala puno manje (tek se nekoliko °C lokalno povisi temperatura tretiranog uzorka) pa nema nikakve termalne štete. Obrade plazmenim mlazovima Ar i He izvođene su tako da je mlaz bio usmjeren u jednu točku na površini testne pločice ili da je pločica pomicana u odnosu na mlaz. Obrada uzoraka plazmenim mlazom je beskontaktna (nema mehaničkog kontakta pa time ni mehaničkih oštećenja), a udaljenost plazmenog mlaza od uzorka može utjecati na jačinu međudjelovanja mlaza i površine, čime se može kontrolirati jačina, odnosno učinkovitost obrade. Beskontaktni hladni atmosferski plazmeni mlaz omogućio bi sigurniju obradu drvenih umjetnina kao alternativa uporabi metil-bromida, alkohola (etanol) i mehaničkog uklanjanja mikroorganizama. Ideja je da se plazmenim mlazom uklanjaju nečistoće s površina (procesima jetkanja s pomoću kisikovih radikala) i deaktiviraju mikroorganizmi, kao što su gljivice, budući da je plazmeni mlaz kemijski vrlo aktivan (MOUNIR LAROUSSI, 2002) (UV svjetlo, radikali, ozon, peroksid). Također se ispitivala mogućnost uklanjanja stratigrafskih slojeva oslika testnih pločica. Pri uklanjanju stratigrafskih slojeva udaljenost mlaza bila je 0,5 cm i s duljim djelovanjem na jednu točku na površini, za razliku od obrade dezinfekcije u kojoj je udaljenost bila 1 – 1,5 cm sa znatno kraćim vremenskim djelovanjem na jednu točku. U prvom dijelu projekta za ispitivanje uklanjanja stratigrafskih slojeva oslika izrađeno je 12 posrebrenih i 12 pozlaćenih pločica (dimenzija 3 cm x 3 cm x 2 cm). Metalizacija je izrađena samo na gornjoj stranici pločica. Testne pločice su dodatno višeslojno oslikane i/ili lakirane, s ciljem da se što vjernije imitiraju višestruki preslici, lakovi i naknadne intervencije koje se često nalaze na pravim umjetninama. Mikrouzorci slikanog sloja pločica uzeti prije i nakon obrade plazmenim mlazom poslužili su za precizniju analizu dobivenih rezultata uklanjanja stratigrafskih slojeva. Nakon probi uklanjanja stratigrafskih slojeva, može se zaključiti da plazmeni izvor nije učinkovit u tu svrhu. Naročito nije moguće uklanjati svaki sloj zasebno. Pri obradi na posrebrenim testnim pločicama primijećeno je da srebrni listić površinski oksidira pri kontaktu s plazmenim mlazom ako nema nikakav zaštitni sloj (npr. lak) na površini. Međutim, primjetna je morfološka promjena tretiranih slojeva na svim testnim pločicama. Te novonastale morfološke promjene laka nakon obrade potrebno je bolje istražiti zbog kemijskih promjena, a time se otvara mogućnost izvođenja novih istraživanja. Zaključeno je da tim tipom plazme nije moguće ukloniti stratigrafski sloj s površine, ali je primjetna morfološka promjena tretiranog sloja. U drugom dijelu projekta ispitivano je djelovanje hladnog plazmenog mlaza u svrhu dezinfekcije drvenih testnih pločica kontaminiranih gljivičnim micelijem. Prije ispitivanja utjecaja plazmenog mlaza na rast gljiva, uspostavljen je sustav uzgoja uzročnika truleži drva, i to vrsta *Coniophora puteana* i vrsta *Serpula lacrymans* na testnim pločicama. U tu svrhu izrađene su pozlaćene testne pločice od tri vrste drva (lipa, smreka, bukva), od kojih su najčešće izrađene drvene polikromirane skulpture na našem području. Utvrđeno je da gljivična vrsta *C. puteana* brže raste u eksperimentalnim uvjetima pa je ona korištena u ispitivanju učinkovitosti plazmenog mlaza na dezinfekciju testnih pločica. Sve tri vrste drva bile su podjednako dobar supstrat za rast gljiva, no u daljnjim pokusima korištena je lipa. Komadići krute hranjive podloge prorasli micelijem naneseni su na testne pločice i smješteni u zatvoreni sustav s visokim sadržajem vlage potrebnim za rast gljivičnih vrsta. Nakon sedam dana pri 18 °C micelij je dovoljno porastao, odnosno prekrio određeni postotak površine pozlaćenih testnih pločica. Taj postotak bio je referentni podatak u odnosu na koji se određivao daljnji rast gljiva nakon obrade. Uzorci su obrađeni različitim vrstama hladne plazme. Nakon obrade, uzorci su vraćeni u sustav na još osam dana kako bi se pratilo je li došlo do oporavka gljivice. Za proučavanje učinkovitosti dezinfekcije testnih pločica kontaminiranih gljivicama vrste *C. puteana* atmosferskim plazmenim mlazom načinjeno je više obrada s tri plina (helij, argon i mješavina 90 % argona i 10 % kisika) i s dvije duljine obrade (dvije minute i pet minuta). Testne pločice su pri obradi pomicane u odnosu na mlaz, kako bi se tretirala cijela gornja površina pločice na kojoj su bile izrasle gljive. Za usporedbu, testne pločice tretirane su alkoholom (96 %-tni etanol) i mehanički (standardna obrada u restauriranju/konzerviranju). Svaka obrada izvodila se na tri testne pločice da se dobiju statistički podaci za kvantizaciju učinkovitosti obrade plazmenim mlazom. Ispitivanje dezinfekcije testnih pločica dalo je pozitivne rezultate, što je bio i glavni cilj projekta. Rezultati ispitivanja pokazali su da je plazmeni mlaz Ar najučinkovitiji, budući da uvjetno nakon prve obrade nije bilo daljnjeg rasta gljivica. Također, plazmeni mlaz Ar/O_2 znatno uspori napredovanje gljivica. Općenito se postiglo da obrada atmosferskim plazmenim mlazom, bez obzira na vrstu plina, daje bolje rezultate nego mehaničko uklanjanje gljivica. Uklanjanje alkoholom (96 %-tni etanol) također se pokazalo vrlo učinkovitim, odnosno potpuno je zaustavilo rast gljivica. Međutim, pri toj obradi pojavila su se i oštećenja na površini testne pločice, što je svakako negativan učinak. Iako bi bilo dobro nastaviti i proširiti ispitivanje, dobiveni rezultati upućuju na mogućnost korištenja atmosferskog hladnog plazmenog mlaza u svrhu dezinfekcije predmeta od drva. Na kraju se može zaključiti da je projekt otvorio nove mogućnosti istraživanja primjene hladnog atmosferskog plazmenog mlaza u konzerviranju-restauriranju umjetnina. Istraživanja se mogu provoditi, osim na drvu, i na drugim osjetljivim materijalima, kao što su papir i platno, što će biti tema naših budućih interdisciplinarnih istraživanja.

KLJUČNE RIJEČI: *konzerviranje-restauriranje drvenih umjetnina, dezinfekcija, gljivice, hladni atmosferski plazmeni mlaz, plazmene tehnologije, plazmena dezinfekcija, plazmena obrada materijala*