Removal of organic contaminants using plasma at atmospheric pressure

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Στους γονείς μου για τη στήριξή τους όλα αυτά τα χρόνια
Cold plasma is of wide use in textile industry, water purification, surface treatment and medical decontamination\(^1\). The purpose of the experiment was to test the effects of the dielectric barrier discharge in ambient pressure to organic substances deposited on a substrate in order to observe their removal and chemical transformation, with possible applications in the decontamination of medical equipment from pathogenic proteins (prions) which are resistant and require complex methods in order to be deactivated. For this, two organic dyes were used, namely carmoisine (aka azorubine) and Coomassie Brilliant Blue G 250 as well as human hemoglobine as the proof of concept. Films of the aforementioned substances were obtained on regular glass (SiO\(_2\)) substrates by dip coating and left to dry with different times and under different conditions (regular evaporation and accelerated evaporation using dry heat). The transmittance spectra, 10 in number for each substance and dielectric combination, in UV-VIS were obtained for the untreated samples and after each treatment with plasma. The treatment times were not kept constant, but rather depended on the substance and the dielectric used, namely SiO\(_2\) and Al\(_2\)O\(_3\). The measured spectra were converted to absorbance and the integral of the absorbance band was studied as a function of treatment time. This resulted in decreasing behavior, fitted by the sum of two exponential terms\(^2\), one referring to the active molecule deactivation and one to the complete removal of material from the substrate. Also, measurements with FTIR spectroscopy were performed giving an estimation about the molecule presence on the samples with treatment time. Moreover, FTIR was performed on gas samples from the discharge enclosure and N\(_2\)O and O\(_3\) were identified as products of the DBD. Furthermore, plasma characterization measurements were carried out, giving information for the plasma temperature and its content in excited species. The first measurements were carried out with a thermocouple that was attached with regular duct tape to the outside walls of the dielectrics. Moreover, with low resolution optical emission spectra, the vibrational transitions of molecular nitrogen\(^3\) were observed, as expected, since the discharge takes place in atmospheric air. With high resolution spectra, the rotational transitions of the 337.1 nm band head allowed an estimation of the air temperature in the discharge with the use of Boltzmann plots. Current and

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\(^1\)Plasma industrial applications, Thierry USA, https://www.thierry-corp.com/plasma-applications/industrial/


light measurements for different applied voltages also provided with time and intensity information about the discharges.
ΑΠΟΜΑΚΡΥΝΣΗ ΟΡΓΑΝΙΚΩΝ ΚΑΤΑΛΟΙΠΩΝ ΜΕ ΤΗ ΧΡΗΣΗ ΠΛΑΣΜΑΤΟΣ ΣΕ ΑΤΜΟΣΦΑΙΡΙΚΗ ΠΙΕΣΗ - ΠΕΡΙΛΗΨΗ

Το ψυχρό πλάσμα χρησιμοποιείται ευρέως στην βιομηχανία υφασμάτων, την απολύμανση νερού, την μεταβολή των επιφανειακών ιδιοτήτων υλικών και την αποστείρωση τραυμάτων ή εξοπλισμού. Σκοπός του πειράματος ήταν να ελεγχθεί η επίδραση, σε ατμοσφαιρική πίεση, της DBD (εκκένωση διηλεκτρικού φράγματος, η ακριβής απόδοση στα ελληνικά) σε οργανικές ουσίες πάνω σε γυάλινες πλάκες, έτσι ώστε να παρατηρηθούν οι ατμομάκρυνση και χημική μεταβολή τους, με πιθανές εφαρμογές στην απολύμανση υλικών εξοπλισμού από παθογόνες πρωτεϊνές, οι οποίες είναι αρκετά ανθεκτικές και απαιτούν χρονοβόρες και ακριβείς μεθόδους για την αδρανοποίησή τους. Για το λόγο αυτό, δύο οργανικές βαφές χρησιμοποιήθηκαν και συγκεκριμένα καρμοϊζίνη (γνωστή επίσης και ως αζορουμπίνη) και Coomassie Brilliant Blue G 250 όπως επίσης και ανθρώπινη αιμογλοβίνη. Υμένια των προαναφερθέντων ουσιών εναποτέθηκαν πάνω σε γυαλί, με την τοποθέτησή του στα εν λόγω διαλύματα και αφήνοντάς το να στεγνώσει με διαφορετικούς χρόνους και υπό διαφορετικές συνθήκες (εξάτμιση και χρησιμοποιώντας ένα πιστολάκι για τα μαλλιά του εμπορίου). Λήφθηκαν τα φάσματα διαπερατότητας στο ορατό-υπεριώδες των αρχικών δειγμάτων (10 για κάθε συνδυασμό που αναφέρεται παρακάτω) και έπειτα από κάθε ακτινοβόληση με πλάσμα. Οι χρόνοι ακτινοβόλησης δεν κρατήθηκαν σταθεροί, αλλά εξαρτούνταν από την ουσία και το διηλεκτρικό (διοξείδιο του πυριτίου SiO₂ και οξείδιο του αργιλίου Al₂O₃). Τα φάσματα διαπερατότητας μετατράπηκαν σε φάσματα απορρόφησης και το ολοκλήρωμα της κορυφής μελετήθηκε συναρτήσιμο του χρόνου ακτινοβόλησης. Η παραπάνω μελέτη είχε ως αποτέλεσμα την εμφάνιση φθίνουσας συμπεριφοράς που περιγράφεται από το άθροισμα δύο εκθετικών όρων και οι οποίοι αναφέρονταν, ο ένας στην μεταβολή του ενεργού μορίου λόγω της κορυφής απορρόφησης και ο άλλος στην απομάκρυνση και τον καθαρισμό του υποστρώματος. Στα φάσματα αυτά, οι κορυφές απορρόφησης που αναφέρθηκαν ήταν ευρέιες (περί τα 200 νανόμετρα) και για τις δύο χρωστικές. Κατά την ακτινοβόληση τους με πλάσμα, οι κορυφές μειώνονταν συναρτήσιμο του χρόνου σε σχέση με το υπόβαθρο. Το υπόβαθρο αναφέρεται στην σκέδαση του φωτός λόγω της μη πλήρους απομάκρυνσης των υπολειμμάτων των χρωστικών. Στα φάσματα αυτά, οι κορυφές απορρόφησης που παρατηρήθηκαν ήταν ευρέιες (περί τα 200 νανόμετρα) και για τις δύο χρωστικές. Κατά την ακτινοβόληση τους με πλάσμα, οι κορυφές μειώνονταν συναρτήσιμο του χρόνου σε σχέση με το υπόβαθρο. Το υπόβαθρο αναφέρεται στην σκέδαση του φωτός λόγω της μη πλήρους απομάκρυνσης των υπολειμμάτων των χρωστικών. Οι σταθερές χρόνοι που αναφέρονταν στην μεταβολή των υποστρώματων των χρωστικών αυτών, βρέθηκε για τους συνδυασμούς διηλεκτρικού και χρωστικής, αντίστοιχα: Γυαλί - Καρμοϊζίνη 3,56 δευτερόλεπτα, Γυαλί - Brilliant Blue 15,5 δευτερόλεπτα, Κεραμικό - Καρμοϊζίνη 63,1 δευτερόλεπτα και Κεραμικό - Brilliant Blue
15.5 δευτερόλεπτα. Επίσης, για τον συνδυασμό Γυαλί - Αιμογλοβίνη λήφθηκαν οι χαρακτηριστικοί χρόνοι, οι οποίοι όμως δεν έχουν τόσο ισχυρή σύνδεση με την μεταβολή της ουσίας, λόγω του μικρού πάχους του υμενίου, και την αδυναμία ακτινοβόλησης με βήμα μικρότερο των 5 δευτερολέπτων. Ενδεικτικά αναφέρεται ότι οι χαρακτηριστικοί χρόνοι της αιμογλοβίνης βρέθηκαν ίσοι με 1,4 δευτερόλεπτα, που αντικατοπτρίζει την λεπτότητα του υμενίου.

Επίσης, πραγματοποιήθηκαν μετρήσεις στο υπέρυθρο παρέχοντας εκτιμήσεις για την παρουσία συγκεκριμένων ομάδων μορίων στα δείγματα συναρτήσει του χρόνου ακτινοβόλησης. Το διηλεκτρικό που χρησιμοποιήθηκε ήταν το γυαλί, ώστε να παρατηρηθεί πιο ομαλά η χημική μεταβολή, σε σχέση με τη χρήση του κεραμικού που παράγει μεγαλύτερη ισχύ. Ενδεικτικά αναφέρεται ότι οι χαρακτηριστικοί χρόνοι της αιμογλοβίνης βρέθηκαν ίσοι με 1,4 δευτερόλεπτα, που αντικατοπτρίζει την λεπτότητα του υμενίου.

Ωστόσο, για την αιμογλοβίνη και για συνολικό χρόνο ακτινοβόλησης 15 δευτερόλεπτα με βήμα 5 δευτερολέπτων, βρέθηκε ότι στα 10 δευτερόλεπτα η κορυφή του αμιδίου ΙΙ εξαφανίζεται, η κορυφή του αμιδίου Ι διευρύνεται και τέλος η κορυφές που αντιστοιχούν στη τάση της ομάδας C-H και του αμιδίου Α εξαφανίζονται. Για ακτινοβόληση του διαλύματος αιμογλοβίνης διάρκειας 15 δευτερολέπτων σε ένα βήμα, οι ίδιες μεταβολές παρατηρήθηκαν. Για την καρμοϊζίνη, λήφθηκαν δύο φάσματα στο υπέρυθρο, το ένα σε περιοχή του γυαλιού όπου το υμένιο ήταν πιο λεπτό και το άλλο εκεί όπου το υμένιο ήταν πιο παχύ. Στο φάσμα του λεπτού υμενίου παρατηρήθηκε η αύξηση μιας ιδιόμορφης κορυφής στα 1354 cm⁻¹ η οποία και αποδόθηκε στη διάσταση του νατρίου που βρίσκεται στα άκρα του μορίου και την δημιουργία νιτρώδους νατρίου (NaNO₂). Στο φάσμα του παχέου υμενίου, παρατηρήθηκε επίσης αύξηση μιας κορυφής στα 836 cm⁻¹ η οποία αποτελεί επίσης την διάσταση του νατρίου που βρίσκεται στα άκρα του μορίου, ενισχύοντας την προηγούμενη σύνδεση της αύξησής του συναρτήσει του χρόνου ακτινοβόλησης. Επιπλέον, μετρήθηκε η θερμοκρασία με τη χρήση θερμοζεύγου στα άκρα των διατάξεων. Από την εξίσωση διάδοσης θερμότητας και τις αντίστοιχες παραδοχές, ήταν δυνατό να συνδεθεί η παράγωγη της θερμοκρασίας που μετρήθηκε με την παράγωγη της θερμοκρασίας στο εσωτερικό των διηλεκτρικών πλακών. Αυτό που παρατηρήθηκε είναι ότι μετά από συγκεκριμένους χρόνους, η θερμοκρασία αυξάνεται με σταθερού ρυθμό.
τις ίδιες κορυφές που παρατηρήθηκαν για το γυαλί. Με χρήση οπτικής φασματοσκοπίας υψηλής ανάλυσης, παρατηρήθηκαν τα επίπεδα της περιστροφικής ενέργειας για την δονήτικη μετάπτωση των 337 νανομέτρων, τα οποία και επέτρεψαν, με τις παραδοχές ότι αυτά καταλαμβάνονται σύμφωνα με την στατιστική Maxwell-Boltzmann και ότι περιστροφική θερμοκρασία των μορίων είναι ίση με την κινητική τους, να εκτιμηθεί η θερμοκρασία του αέρα στο εσωτερικό των πλακών. Τα αποτελέσματα, είναι (σε βαθμούς Κελσίου), 104 για το γυαλί και 234 για το κεραμικό.

Τέλος, με τη χρήση μαγνητομέτρου και ενός κυκλώματος ανάστροφα πολωμένης φωτοδιόδου και οπτικής ίνας που οδηγούσε το σήμα, λήφθηκαν μετρήσεις που αφορούσαν τις χρονικές διάρκειες των κυματοπακέτων και των επι μέρους παλμών οι οποίοι συνδέονται με τους χροσσούς (filaments, streamers όπως εμφανίζονται στην βιβλιογραφία) που λειτουργούν ως κανάλια για την μεταφορά ρεύματος μεταξύ των διηλεκτρικών. Ταυτοποιήθηκαν για τα δύο διηλεκτρικά, δύο τάσεις "καταφλιών", στα 3 kV P-P για το γυαλί και στα 2,5 kV P-P για το κεραμικό, στις οποίες η περίοδος των κυματοπακέτων που περιέχουν τους παλμούς έφτανε και παρέμεινε, για μεγαλύτερες τάσεις, ίση με 100 Hz, διπλάσια δηλαδή της συχνότητας του ηλεκτρικού δίκτυου στην Ρουμανία. Η συχνότητα εμφάνισης των παλμών, φτάνει ένα αντίστοιχο πλατό, μια δυνατοτήτα λιγότερο των παραπάνω τάσεων, και είναι ίση με 56,6 kHz. Σημειώνεται ότι υπάρχει αντίστοιχη ταύτιση των συχνοτήτων εμφάνισης παλμόν και ρεύματος, όπως είναι αναμενόμενο αν πρόκειται να περιγράψουμε τους χροσσούς (filaments). Η μέση ένταση των κορυφών και για τα δύο διηλεκτρικά, κυμαίνεται περί τα 0,1 Amperes για όλες τις τάσεις τροφοδοσίας. Οι κορυφές αντιστοιχούν σε διαιρέσεις των παλμών σύμφωνα με την ακρίβεια του παλμογράφου με την οποία λήφθηκαν. Ο ηλεκτρικός χαρακτηρισμός του πλάσματος, μπορεί να δώσει πληροφορίες για την ισχύ της εκκένωσης σε διαφορετικές τάσεις, ώστε να υπάρχει η αντίστοιχη προσαρμογή στις ανάγκες της ουσίας και του απολυμενόμενου υλικού.

Συνοψίζοντας, η αποτελεσματικότητα του DBD πλάσματος χρίνεται εκανονιστική για την απολύμανση γυαλιού από οργανικές ουσίες με την ανάγκη πρόσθετων ελέγχων για την βελτιστοποίηση και την εφαρμογή του σε πραγματικές συνθήκες.
DBD πλάσμα με γυαλί (κρισταλλί) και με κεραμικό (δεξιά). Οι χρωστικοί (filaments) είναι ορατοί για την περίπτωση του γυαλιού αλλά όχι για το κεραμικό, λόγω του μεγάλου αριθμού τους.

Μεταβολή του ολοκλήρωματος των χρωμάτων απορρόφησης συναρτήσει του χρόνου ακτινοβόλησης, για τους συνδυασμούς των χρωστικών και των διηλεκτρικών.
(a) Κυματοπακέτα ρεύματος για το κεραμικό

(b) Κυματοπακέτα φωτός για το κεραμικό

(c) Κυματοπακέτα ρεύματος για το γυαλί

(d) Κυματοπακέτα φωτός για το γυαλί

Χρονικές πληροφορίες για την διάρκεια, περίοδο και διαφορά μεταξύ των κυματοπακέτων ρεύματος και φωτός για τα δύο διηλεκτρικά συναρτήσει της εφαρμοζόμενης τάσης (P-P)
Φάσματα οπτικής εκπομπής για το γυαλί (a) και το κεραμικό (b)
Φάσματα οπτικής εκπομπής υψηλής ανάλυσης και διαγράμματα Boltzmann: a), c) Γυαλί, b), d) Κεραμικό
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Iași, July 2018
Ilias Machairas
1.1 Plasma & Dielectric Barrier Discharge

The definition of plasma, is the state of matter that consists of positive and negative ions. It is a mixture of the electronic and positive ion gases, which do not have compulsory the same temperature. That would be the case in the sun where the plasma is isothermal, but for the dielectric barrier discharges this is not the case. What makes plasma different from a neutral gas is its collective behavior.

Some basic parameters referring to plasma are the ionization degree, densities of its constituents (electrons, ions, radicals), temperature and Debye length. Starting from the densities, they are simply the number of the specific constituent (electrons, ions, radicals or neutral atoms) in a volume, commonly measured in cm$^{-3}$ for laboratory plasmas and in m$^{-3}$ for stars and big scale plasmas in general. The ionization degree is defined as the number of ions over the sum of ions and neutral species ($a = n_i/(n_i + n_n)$). The temperatures in cold plasmas can reach, for the electrons, several thousand Kelvins but due to non-equilibrium, as their masses are low and they cannot transfer easily their energy to heavier species(ions and atoms), the gas temperature is equal to that of its environment. Finally, the Debye-Hückel length describes the charge separation of the ions and the electrons and is given by the equation:

$$\lambda_D = \left(\frac{\epsilon_0 k_B T_e}{e^2 n_e}\right)^{\frac{1}{2}}$$

(1.1)

Depending on the parameters of the ions, it is possible to obtain the Debye length by substituting their temperature and their density in the above equation (obviously for singly ionized ions, $n_e = n_i$).
In a neutral gas, the interaction between the constituents follows the Van der Waals law which means a decrease of the interaction intensity between two constituents proportionally to \( r^{-6} \), whereas in plasma the interaction follows the Coulomb law; that means the interaction intensity is decreasing proportionally to the inverse square of the distance. This results in each constituent to interact with more of its neighbors and this gives rise to the aforementioned collective behavior.

In this experiment, the plasma used for the surface cleaning is non-equilibrium (cold) and at atmospheric pressure. The pressure defines the voltage to which the gas breakdown takes place. For higher pressures a higher voltage is required, if the gap is maintained constant. In the case of atmospheric plasmas, a voltage in the order of kilovolts is required. The whole system which is depicted in Figure 1.1 acts as a capacitor and therefore, an AC is required in order to have any type of conduction other than displacement current. Furthermore, the use of dielectric is to reduce the current in order for the discharge not to enter the arc region as depicted in Figure 1.2. For our DBD configuration, the current was limited in any case by the source to a maximum value of 20 mA. In general, the

![Figure 1.1: Parallel-plate dielectric barrier discharge schematic, Source: Plasma Science and Technology for Emerging Economies An AAAPT Experience, Rajdeep Singh Rawat, Springer Nature Singapore Pte Ltd., 2017, ISBN 978-981-10-4216-4](image)

DBD can be divided in two categories. The first and studied here is called the filamentary mode, it consists of a number of micro-discharges, called streamers (or filaments) which present a chaotic spatial distribution\(^3\), whereas the second is the homogeneous working mode reported for pressures of 3 kPa\(^4\). Both of the modes are apperking in Figure 1.3.

\(^3\)Overview of Atmospheric Pressure Discharges Producing Nonthermal Plasma, A. P. Napartovich, Plasmas and Polymers, Vol. 6, Nos. 1/2, June 2001

\(^4\)Comparison of surface modification of polypropylene film by filamentary DBD at atmospheric pressure and homogeneous DBD at medium pressure in air, Z. Fang, X. Xie, J. Li, H. Yang, Y. Qiu, E. Kuffel, Journal of Physics D: Applied Physics, Volume 42, Number 8, 2009
These streamers are responsible for current conveyance and they are similar to transient high pressure glow discharges\(^5\).

In Fig. 1.4, the waveforms for the two discharges (homogenous and filamentary) shown in Fig. 1.3, are visible.

Figure 1.4: Voltage and current waveforms for the homogenous (a) and the filamentary (b) DBD, Source: The Use of the Spectrometric Technique FTIR-ATR to Examine the Polymers Surface, Wieslawa Urbaniak-Domagala, http://dx.doi.org/10.5772/48143
1.2 Plasma Decontamination

Cold plasma is used for many years for decontamination purposes. Decontamination does not refer only to pathogenic proteins, bacteria or viruses. A good example is the samples that are studied with the use of transmission electron microscopy (TEM). Because of the nature of its function, the sample has to be very thin, about 50 nm, since otherwise the electrons cannot be transmitted through it. The thin specimens, after they are prepared and before their insertion to the TEM, are treated for some minutes with plasma in a very low pressure (0.1 ∼ 1 Pa) with the working gas being Ar, O₂ or N₂. This is done in order for any impurities that were deposited on the film (even the CO₂ because of the personnel’s respiration!) to be removed and obtain the optimal signal possible during the microscopy. Another example refers to water treatment. There are already industrial and home systems⁶ that are used to treat the water with ozone which is produced by corona discharges. Ozone, as a highly reactive species, oxidizes and deactivates potentially harmful substances and is as well toxic for living organisms (in that case the interest is about the pathogenic microorganisms such as spores, biofilms, yeast; for a complete list of relative research refer to the Plasma for Bio-Decontamination, Medicine and Food Security, Springer, 2012, ISBN 978-94-007-2852-3). Specifically, this is because of the easy oxidization of lipids and membrane proteins of the cells⁷. Regarding medical equipment, the DBD is used to activate the surfaces of tubes, syringes etc.⁸ which is contained in the wider surface treatment with plasma⁹, to make a surface more hydrophilic for example. Regarding the decontamination, Rossi et al.¹⁰ reported that they achieved sterilization from spores (see Fig. 1.5, deactivation of lipopolysaccharides (endotoxins) and protein film removal. What has to be noted is that the maximum pressure used was not more than 133 Pa, three orders of magnitude smaller than the atmospheric pressure. In 2015, Bandow et al.¹¹ reported that a dielectric barrier discharge in atmospheric pressure managed to inactivate one protein in the most stable protein family in nature. The literature of the field is very rich, but based on the last work mentioned, the idea of using a dielectric barrier discharge in atmospheric pressure seems very attractive. That is because the cost of the assembly and its function is very cheap. The assembly consists of two electrodes, the dielectric and the high voltage source; no expensive vacuum chamber is required nor specialized personnel to operate it. A drawback could be the HV hazard and the gas exhaust content (O₃, NOₓ), that might need further treatment to reduce the level of pollutants up to legal limits. This could be compensated also by the fact that since a vacuum chamber is not used, the existence of a treatment line is possible, reducing the treatment times dramatically.

⁶http://www.ozomax.com/
⁷https://earthobservatory.nasa.gov/Features/OzoneWeBreathe/ozone_we_breathe3.php
¹⁰Decontamination of Surfaces by Low Pressure Plasma Discharges, 2006, DOI: 10.1002/ppap.200600011
¹¹A dielectric barrier discharge terminally inactivates RNase A by oxidizing sulfur-containing amino acids and breaking structural disulfide bonds, 2015, doi:10.1088/0022-3727/48/49/494003
Finally, an important fact that has to be addressed, is that the temperatures for large times of treatment have been observed to be unsuitable for some materials (artificial polymers for example). In every possible application, the temperature should be kept within the limits that the specific material allows.

Figure 1.5: SEM pictures of treated spores in different gas mixtures and estimation of their lengths: (A) pure N\textsubscript{2}; (B) O\textsubscript{2} / N\textsubscript{2} 20:80; (C) pure O\textsubscript{2} (treatment time 10 min, power 500 W, 20DC, 5 ms time on, 13.3 Pa, 10 sccm), Decontamination of Surfaces by Low Pressure Plasma Discharges, Rossi et. al, 2006
1.3 Spectroscopy Basics

The studies performed for the purposes of the thesis, heavily relied on the detection of electromagnetic radiation in UV-VIS and IR ranges. As a result, a basic description of the processes resulting in the final forms of the spectra obtained and studied seems necessary and useful for the completeness of this work. Starting from the spectra obtained in the UV-VIS range, an example is shown in Fig. 1.6.

![Hemoglobin absorbance spectrum](image)

Figure 1.6: Hemoglobin absorbance spectrum obtained for the study of the substance kinetics due to DBD plasma treatment

This wide band is due to many processes taking place while the radiation interacts with the molecule under study. Firstly, when the molecule is a complex organic one with many chemical groups, these can absorb at many appropriate wavelengths which due to the resolution of the experimental apparatus are overlapping, causing a broadening of the FWHM and a shift of the peak. The shift can be also caused by the "chain" interaction of one group which absorbed light with its immediate neighbors. The third important process, is that of the electronic transition energy levels splitting due to additional quantum numbers referring to the vibration and rotation of the molecule. Because of the relative small ratio of these additional energies over the one of the electronic transition, they are treated as a small perturbation allowing the adiabatic approximation (Born-Oppenheimer) to be used:

$$E_{tot} = E_n + E_{vib} + E_{rot}$$  (1.2)
The orders of magnitude of the rotational energies\textsuperscript{12}, the vibrational (Table 1.1) and the electronic, are as follow:

\[ E_n \sim 1 \text{ eV} \] (1.3a)
\[ E_{vib} \sim 10^{-3} - 1 \text{ eV} \] (1.3b)
\[ E_{rot} \sim 10^{-6} - 10^{-2} \text{ eV} \] (1.3c)

It is possible then to have a wavelength shift (which finally is the reason for the wide band):

\[ \Delta \lambda \sim 10^{-4} - 10^{2} \text{ nm} \] (1.3d)

All of the above reasons contribute to the wide band appearing in the UV-VIS spectra and whose integral is studied as a function of treatment time to measure the existence of the particular substance on the substrate and finally the efficiency of plasma regarding substance removal or chemical transformation.

In IR spectroscopy, causes of the peak displacement and widening are the skeletal effect, which alters the energy levels of the free chemical group when it is bound to a larger molecule and solvent effects\textsuperscript{13} which cause blue shifts for the \( n \to \pi^* \) transitions and red shifts for the \( \pi \to \pi^* \) transitions. Infrared spectroscopy requires that the molecules have a dipole moment and the transitions that are observed in the IR region are the vibrational.

Vibrational transitions were also used to identify the species in the plasma discharge by using an optical emission spectroscopy system. This resulted for the presence of the second positive system of molecular nitrogen to be identified. Rotational spectra were also obtained for the 337.1 nm head (vibrational transition) of \( \text{N}_2 \) which contain blue-shifted lines due to the addition of the rotational energies and which were used for an estimation of the gas temperature inside the discharge with the use of the Boltzmann plot. By considering that the rotational temperature is equal to that of the gas, which is approximately true for non-isothermal plasmas, and that the rotational levels of a single vibrational transition are occupied according to a Boltzmann distribution, it is possible for an equation of the form to be obtained\textsuperscript{14}:

\[ \ln \frac{I_{J'}}{J' + 1} = \frac{B_e J' (J' + 1)}{k_B T_R} + C \] (1.4)

where \( J \) is the quantum number corresponding to the initial state and \( J' \) the quantum number corresponding to the final. The \( J' + 1 \) in the logarithm corresponds to a factor which contains the rotational degeneration and spin orbit coupling and is equal to the

\textsuperscript{14}http://www.fch.vut.cz/~krcma/vyuka/plazma/3-oes-en.pdf
above value only for the simplest of cases (single transition, $\Delta L = 0$). As a result, by measuring the intensities and assigning the peaks to the rotational levels, the graph can be fitted with a straight line from whose slope the rotational temperature (and so approximately) the gas temperature can be calculated. It is noted that in the relevant section, the x axis has units of $(J' + 1)(J'' + 2)$. This is because the peaks selected from the rotational spectra corresponded to a $\Delta J = 2$. More information about molecular spectroscopy can be found in the book of Wolfgang Demtröder, *Atoms, Molecules and Photons, Springer* and specifically for the rotational spectra in the chapter *Diatomic molecules* of the above book.

![Image of energy levels](image)

**Figure 1.7:** The change in energy when molecular vibrations and rotations are considered. *Source: Wolfgang Demtröder, Atoms, Molecules and Photons, Springer*

The graph above shows the splitting of the electronic energy states because of vibrations and the splitting of the vibration energy states because of rotations. In low resolution experimental apparatus, these levels appear as continuous bands (UV-VIS), but in high resolution for example, their separation is visible. In the next figure, a high resolution optical emission spectrum is visible (along with the respective simulation) where the aforementioned separation is shown.
Figure 1.8: High resolution optical emission spectrum and simulation for a plasma discharge in $10^5$ Pa of argon. Dahle, Sebastian and Hirschberg, J and Viöl, Wolfgang and Maus-Friedrichs, Wolfgang. (2015). Gas purification by the plasma-oxidation of a rotating sacrificial electrode. Plasma Sources Science and Technology. 24. 10.1088/0963-0252/24/3/035021.
1.4 FTIR Spectroscopy

Infrared spectroscopy is a very important technique used by scientists to gain information about substances in any state of matter, gas, liquid or solid, by using the fact that vibrational and rotational excitations of molecules take place in this energy region, namely 1.24 meV - 1.58 eV. It is customary in IR spectroscopy for the reduced wavenumber to be used and which is measured in cm\(^{-1}\) \((\nu = 1/\lambda)\). The region of the infrared is divided to three sub-regions, the far infrared, the mid infrared and the near infrared. More detailed information appears in Table 1.1.

![Table 1.1: Infrared spectrum subranges and relative information, Source: http://halas.rice.edu/conversions](http://halas.rice.edu/conversions)

<table>
<thead>
<tr>
<th>Subrange</th>
<th>Abbreviation</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near Infrared</td>
<td>NIR, IR-A</td>
<td>1.58 - 0.886</td>
<td>780 - 1400</td>
<td>12800 - 7140</td>
</tr>
<tr>
<td></td>
<td>NIR, IR-B</td>
<td>0.886 - 0.413</td>
<td>1400 - 3000</td>
<td>7140 - 3330</td>
</tr>
<tr>
<td>Mid Infrared</td>
<td>MIR, IR-C</td>
<td>413 - 24.8 meV</td>
<td>3 - 50 µm</td>
<td>3330 - 200</td>
</tr>
<tr>
<td>Far Infrared</td>
<td>FIR, IR-C</td>
<td>24.8 - 1.24 meV</td>
<td>50 µm - 1 mm</td>
<td>200 - 10</td>
</tr>
</tbody>
</table>

In the past, the IR spectroscopy was carried out using dispersive elements such as prisms. With the development of the computers, the process became faster, because the interferogram could be measured and be transformed to the respective spectrum using the Fourier transform, therefore giving the name of FTIR spectroscopy to the method used nowadays. The function of FTIR spectroscopy is simply given as follows. For a monochromatic light source, the beam before the sample and the detector goes through a Michelson interferometer. Depending on the displacement of the movable mirror, a maximum intensity is detected for a zero path difference (ZPD), whereas it varies with the movement of the mirror, giving a graph like the one in Fig. 1.9a, of intensity over optical path difference (OPD). If a source that is emitting in a wide region of the IR spectrum is used, the form of the interferogram is more complex (Fig.1.9b). After the interferometer is generated, it is converted to the respected spectrum, using the well established, mathematically, Fourier transform. This is the basic principle with which the FTIR spectra are obtained and allow the quantitative and qualitative analysis of samples.

The FTIR spectroscopy utilizes several methods depending on whether the reflected or the transmitted light is measured. For the purposes of the experiment, the transmission method was used in order for the species in the gas environment of the discharge to be identified and the attenuated total reflectance (ATR) for the study of the dye and protein samples. For the gas measurements, a vacuum cell was used, with KBr windows which are transparent to the infrared light. For the dye and protein samples, because they were deposited on regular glass substrates, which are not transparent, ATR spectroscopy was used and it is described briefly in the next subsection.
1.4.1 Attenuated Total Reflectance (ATR-IR) Spectroscopy

This type of spectroscopy utilizes the reflection that is taking place on a separating surface between an optical denser crystal (ZnSe in the experiment) and the sample, when the light hits the surface with an angle greater than the critical. The contact between the sample and the crystal has to be tight enough and this is accomplished by a metallic pin that presses them together. This crystal functions as a prism leading the incident radiation to the sample and to the detector after the reflection has occurred. Because of the field continuity is required, this gives rise to a very fast decreasing wave called evanescent wave\(^{15}\) and which is perpendicular to the separating surface. When the sample selectively absorbs at some frequency, energy is lost for this particular frequency from the reflected beam which is finally measured by the detector and leads to the final spectrum. Fig. 1.10 shows the schematic of the above process and with this concludes the paragraph.

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\(^{15}\)The Use of the Spectrometric Technique FTIR-ATR to Examine the Polymers Surface, Wieslawa Urbaniak-Domagala, http://dx.doi.org/10.5772/48143
Chapter 2

Experimental Part

2.1 The experimental setup and UV - VIS diagnostics of the decontamination

The core of the experiment was the dielectric barrier discharge and its effect on the films of organic substances. It is therefore important the schematic presentation of the main experimental setup. In the images below, this setup is shown along with blocks that correspond to the experimental instruments used with their special characteristics. This was done in order for their concrete presentation and to be collected in a common page, in addition to mentioning them in the relevant sections. Starting from Fig. 2.1, the equipment used is shown along with the necessary parameters of the dielectric barrier devices. In Fig. 2.2, the setup used for the treatment of the samples is shown. This schematic is explained as follows: Because of the increasing ozone level after some minutes of treatment, a hollow box of EPS (expanded polystyrene) was used with two fans and a pump system to lead the produced ozone outside the laboratory. To prevent as much as possible the escape of ozone in the laboratory, a transparent plastic enclosure was used to cover the DBD and the fans (in contrast with the schematic where the enclosure does not seem to cover the fans totally). On its top, a small hole with a diameter of about 2 cm was opened in order to keep a normal air flow. This setup worked sufficiently well, but still after some minutes of discharge, the ozone in the laboratory would accumulate. Ozone evacuation is a problem that should be seriously considered in DBD setups at atmospheric pressure. In Fig. 2.3, the two discharges for 5.5 kV\textsubscript{P-P} and 3 kV\textsubscript{P-P}, for the ceramic and the glass DBDs appear respectively. In the glass discharge, the filaments appear clearly, whereas in the ceramic discharge, the filaments were not captured properly, because of their large number, appearing as a continuously distributed light, but this is not the case. The image presented in Fig. 2.3, is quantitatively described in Section 2.6 (Current and Light measurements).
Figure 2.1: Instrumentation used for the experiments
2.1. The experimental setup and UV - VIS diagnostics of the decontamination

![Schematic of the main experimental setup](image)

**Figure 2.2: Schematic of the main experimental setup**

The main tests were conducted using spectroscopy in the UV - VIS domain. The function of the spectrograph is based on the transmittance of the light beam through the samples and through the substrate which serves as a reference in this case. Before these measurements, a baseline measurement is performed with the lid of the spectrometer open, in order for the noise, which is due to the environment, to be canceled out. This last measurement is performed every time that the spectrograph is put in function. Regarding the actual beams, for a specific wavelength, the two intensities are registered and by their ratio, the transmittance spectrum is plotted. It is then possible for the
Experimental Part

Figure 2.3: a) The glass DBD, b) The ceramic DBD. The filaments are visible in the glass discharge, but not in the ceramic, because of their large number absorbance spectrum to be derived using the Beer-Lambert law:

\[ A = -\log\left( \frac{T}{T_0} \right) \]  

(2.1.0.1)

In the above equation, \( T_0 \) refers to the transmittance of the substrate in each wavelength.

Figure 2.4: Schematic of transmittance through the samples

The measurements were carried out with the use of the Evolution 300 UV-Vis Spectrophotometer produced by Thermo Fisher\(^1\). The parameters used in VISION (the spectrometer software) were as follows:

- Scanning Speed: 1200 nm/min
- Bandwidth: 2 nm

\(^1\)https://www.thermofisher.com/order/catalog/product/10300101
2.1. The experimental setup and UV - VIS diagnostics of the decontamination

- Mode: % Transmittance

The bandwidth also modified the surface illuminated, and the 2 nm were chosen as the optimal value. The voltages used to spike the discharge were $3.0 \pm 0.5$ kV p-p for the glass dielectric and $5.5 \pm 0.5$ kV p-p for the ceramic for all three substances under study.

2.1.1 Colorants - Carmoisine & Coomassie Brilliant Blue G-250

The first organic substance to be used, is carmoisine\(^2\) (also known by the name azorubine or E122), an azodye used in food colorants with a deep red color and the formula\(^3\) $C_{20}H_{12}N_2Na_2O_7S_2$. Specifically, carmoisine was soluted in water along with sodium benzoate\(^4\) ($C_6H_5COONa$) which serves as a conservative and existed already in the product. The colorant was produced by the company under the name: "s.c.m. colin daily". The second colorant was a laboratory prepared solution with Coomassie Brilliant Blue G-250, produced by FLUKA. The glass substrates used were produced by Deltalab\(^5\), and had dimensions of 26x76x1 mm.

Films of the above dyes were obtained by dip coating. The regular glass substrate was introduced into the solution, remained for different times, removed and left to dry also with different times, until a clearly visible dry film could be observed. The following films showed a strong absorbance band which was being reduced progressively with treatment time, following a second order exponential decay. For each dye and each dielectric, ten sets of measurements were obtained. Then, the time evolution of the integral of the peak with an individual linear baseline was studied in order to quantify the chemical

\(^{2}\)https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/azorubine
\(^{5}\)http://www.deltalab.es/en/producto/eurotubo-slides/
change/removal of the dyes. The following four graphs are indicative of the time evolution of the samples under treatment.

Figure 2.6: Brilliant Blue G250 spectra for the glass DBD treatment

Figure 2.7: Brilliant Blue G250 spectra for the ceramic DBD treatment
2.1. The experimental setup and UV - VIS diagnostics of the decontamination

Figure 2.8: Carmoisine spectra for the glass DBD treatment

Figure 2.9: Carmoisine spectra for the ceramic DBD treatment
The above graphs were generated with the use of Spectragryph\textsuperscript{6}. The .txt files from VISION were imported, and each spectrum was normalized to the glass substrate spectrum. After that, all spectra were changed to absorbance with the use of software built-in functions (also verified manually) and finally, for intervals depending on the substance, the integrals of the bands were calculated with individual baselines referring to scattering effects, being substracted from the above summation.

\textbf{Figure 2.10:} Absorbance in the respective bands evolution as a function of treatment time, for the two DBDs and the two colorants used.

In Tables 2.1-2.4 the integrals that quantify the removal of the active molecules and were used for the above graphs, are shown.

\textsuperscript{6}https://www.effemm2.de/spectragryph/
2.1. The experimental setup and UV - VIS diagnostics of the decontamination

Table 2.1: G250 - Al\(_2\)O\(_3\), Abs. band: 500 - 700 nm, 10 samples

<table>
<thead>
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<th>Time (sec)</th>
<th>Integral (Average)</th>
<th>Integral (Standard Deviation)</th>
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<td>0.63</td>
<td>1.01</td>
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Table 2.2: G250 - SiO\(_2\), Abs. band: 500 - 700 nm, 10 samples

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<th>Time (sec)</th>
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<tr>
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<td>0.62</td>
<td>0.52</td>
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<tr>
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<tr>
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<tr>
<td>300</td>
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Table 2.3: Carmoisine - SiO$_2$, Abs. band: 400 - 640 nm, 10 samples

<table>
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<tr>
<th>Time (min)</th>
<th>Integral (Average)</th>
<th>Integral (Standard Deviation)</th>
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<td>1</td>
<td>3.42</td>
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<td>1.86</td>
<td>1.08</td>
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<tr>
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<tr>
<td>9</td>
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<tr>
<td>10</td>
<td>-0.62</td>
<td>0.82</td>
</tr>
<tr>
<td>11</td>
<td>-0.69</td>
<td>0.81</td>
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<td>0.73</td>
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<tr>
<td>13</td>
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<tr>
<td>14</td>
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Table 2.4: Carmoisine - Al$_2$O$_3$, Abs. band: 400 - 640 nm, 10 samples

<table>
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<th>Time (sec)</th>
<th>Integral (Average)</th>
<th>Integral (Standard Deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>6.67</td>
</tr>
<tr>
<td>10</td>
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<td>5.93</td>
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<td>1.30</td>
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</tr>
<tr>
<td>120</td>
<td>0.94</td>
<td>2.36</td>
</tr>
</tbody>
</table>
It is observed that in all cases, the fit of the two exponentials, describes the data points precisely. For the combination of the ceramic DBD with carmoisine, it is unknown why so large errors appear. A hypothesis is that the power dissipation, which is much larger than the glass DBD, in combination with a larger deviation of the film thickness of the red colorant, causes polymerization faster than molecule deactivation or removal and the inner part of the film is protected from the plasma active species by the outer polymer film. Indeed, for the thick films of the red dye, it was observed that the color after the treatment appears to be towards white, but the substrate is not clean. The above explanation should be tested for a definite conclusion, using supplementary chemical analysis techniques.

### 2.1.2 Hemoglobin Test

After the tests with the organic dyes, ten sets of measurements were also obtained for a hemoglobin solution, obtained by dissolving hemoglobin lyophilized powder (crystals) by SIGMA-ALDRICH in the UV-VIS range. In Fig. 2.11, one of the measurements is displayed for the untreated sample and until 30 seconds treatment with 5 seconds step. It appears that for the particular sample, a 5 second treatment causes the disappearance of the characteristic absorbance band.

![Figure 2.11: Hemoglobin spectra in the VIS range for the untreated solution and after different treatment times](https://www.sigmaaldrich.com/catalog/product/sigma/h7379)

Figure 2.11: Hemoglobin spectra in the VIS range for the untreated solution and after different treatment times

For the range 380-460 nm, the band integral with an individual linear baseline was plotted as a function of treatment time. The resulted graph is displayed in Fig. 2.12.
The fit of the integral points is indicative, because of the film being thin and the peak vanishing after 5 seconds treatment. In order to study the kinetics properly, treatment times of one or half a second should be obtained, so that in the $0 \rightarrow 5$ seconds interval there would be more points to give information about the reduction of hemoglobin. This could be achieved by controlling the source through a computer. Nevertheless, it can be safely concluded that the hemoglobin was totally deactivated after 10 seconds of plasma treatment with the $\text{SiO}_2$ DBD.

![Figure 2.12: Band reduction in the range of 380-460 nm of hemoglobin in respect to the exposure time in the glass DBD](image)
2.2 FTIR diagnostics of the decontamination

In addition to the UV-VIS spectroscopy, FTIR analysis has also been performed for the two organic molecules and the hemoglobin solution. The spectrograph used was the JASCO FT/IR-4700, in ATR mode with ZnSe crystal (PKS-Z1), 4 cm\(^{-1}\) resolution. The DBD used for the FTIR studies was the glass one with working voltage of 3.0 ± 0.5 kV, because of its smaller power output, so that the evolution of the molecules could be observed properly. For the organic dyes, two sets of measurements have been performed for each one in order to study the above evolution of their chemical composition; one on the center of the substrate where the film was thinner and one at a specified point where the thickness of the film was larger. This was due to the non-homogenous films that were obtained with the method used. In Fig. 2.13, the film of the carmoisine solution is shown, with the spots placed on the ATR crystal marked.

![Figure 2.13: Treated red film: The black circle corresponds to the thicker part of the film studied with FTIR and the yellow circle corresponds to the thinner film](image)

The first observation of the above sample, is that the dye is not removed after treatment. In the yellow circle region, the color appears to be towards white and relatively transparent in comparison with the lower part, which leads to the conclusion of having
a chemical transformation of the molecule along with partial removal. The region of the black circle appears with a thick red color that is due to the reduced efficiency of the discharge for the particular film and the reduced power near the edges of the DBD.

Figure 2.14: Carmoisine FTIR spectra for different times of treatment. a) The thinner ”white” film, b) The thick red film

The evolution observed by the above spectra refers to the rise of the 1350 cm$^{-1}$ and the 836 cm$^{-1}$ bands. In Fig. 2.14b, the spectrum of the sodium nitrate$^8$ (N$\text{NaO}_2$) also appears for comparison. The rise of these two peaks could be attributed to the appearance of the

$^8$https://webbook.nist.gov/cgi/cbook.cgi?ID=B6007909&Units=SI&Mask=80#IR-Spec, COBLENTZ NO. 7909, Coblentz Society
above substance in the film. In Fig. 2.5a (UV-VIS diagnostics section), there are two ionic bonds of Na with oxygen on the outer parts of the molecule. From the reactive species that were identified from the optical emission spectroscopy (refer Section 2.5), namely N₂O and O₃, and with the respective FTIR spectra, the hypothesis of the formation of the above salt is valid. If that is the case, then sodium is disassociated from the rest of the molecule, maybe with one or two atoms of oxygen in order to produce the sodium nitrate. What could also contribute to the formation of sodium nitrate is the sodium benzoate which existed as a conservative, to be disintegrated, leaving free sodium ions in the film. In any case, chemical transformation is observed and this is equivalent to the deactivation of the original molecule(s).

For the Coomassie Brilliant Blue G250, in Fig. 2.15b, the films before and after the treatment can be observed, as well as a spot where the film was thicker and which, after the treatment, appeared darker.

![Figure 2.15: Brilliant Blue films. a) Untreated sample and b) treated sample. In b it can be seen the darker spot where the film was thicker](image)
The removal of the dye from the substrate is obvious. The FTIR spectra for the blue dye appear in Fig. 2.16.

![FTIR spectra](image)

Figure 2.16: Brilliant Blue FTIR spectra for different times of treatment. a) Spectra in the center of the substrate, b) Spectra of the darker spot

For Fig. 2.16a, the peaks at 1584, 1508 and 1343 cm\(^{-1}\) vanish by the end of the treatment (30 seconds), whereas in Fig. 2.16b they progressively increase. These bands are assigned to the following substances according to the references given in NIST Chemistry Webbook:\(^9\):

1. 1343 cm\(^{-1}\) → 1350 ± 50 cm\(^{-1}\), NH\(_2\)^+ Bend, reported\(^{10}\) using photoelectron spectroscopy of transient species. Part 11. The NH2(X(2)B1) radical, Mol. Phys., 1980, 39, 1121

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\(^9\)https://webbook.nist.gov/

2.2. FTIR diagnostics of the decontamination

troscopy.

2. $1508 \text{ cm}^{-1} \rightarrow 1499 \text{ cm}^{-1}$, H$_2$N Bend, reported\textsuperscript{11} using IR spectroscopy.

3. $1584 \text{ cm}^{-1} \rightarrow 1600 \text{ cm}^{-1}$ C-C stretches of C$_6$ ring.

In Fig. 2.17 appears the molecule of the brilliant blue.

![Brilliant Blue G250 molecule](https://www.sigmaaldrich.com/catalog/product/sigma/27815)

Figure 2.17: Brilliant Blue G250 molecule. Source: https://www.sigmaaldrich.com/catalog/product/sigma/27815

The interpretation of the two sets of spectra is as follows: In Fig. 2.16a, the trace of the molecule vanishes. It is possible, since the molecule is in an aqueous solution for the existence of the NH$_2$ and its ion inside the molecule, in the place of NH. The disappearance of the trace means that the dye is removed, as it is also apparent from Fig. 2.15b. In Fig. 2.16b, the increase of these molecules can be interpreted by the disintegration of the molecule, leaving behind unbound aromatic rings, NH$_2$ and NH$_2^+$.

The final FTIR measurements were performed for the hemoglobin solution. Two sets of spectra were obtained, one for total treatment time of 15 seconds with 5 seconds step and one for 15 seconds in one step. The resulting spectra appear in Fig. 2.18. In the first graph, an FTIR spectrum is also shown for the hemoglobin crystals, where the peaks of the amides appear clearly. In the untreated spectrum, the amide I and II peaks are visible and also the peaks of amide A are slightly apparent. After the treatment of 15 seconds in one step, the amide A peaks are not any more visible in the wider absorbance interval, while also the amide I peak is widened and the amide II peak disappears. In Fig. 2.18b, in 10 seconds, the amide A peaks are widened, almost beyond distinction, the amide I peak is also widened and the amide II peak no longer appears. It is safe

to conclude, by also taking into account the UV-Vis spectra, that for a hemoglobin thin film, the dielectric barrier discharge is efficient in altering the structure of the protein, by mainly destroying the amide II bond. The time necessary for this effect appears to be between 10 and 15 seconds, agreeing with the results in the UV-VIS domain, with the use of the glass DBD. For an additional stage of clearing and disinfection from possibly pathogenic proteins of medical equipment, the glass DBD appears to be effective.

Figure 2.18: FTIR spectra for a hemoglobin solution. a) 15 seconds treatment in one step and the spectrum of the hemoglobin lyophilized powder, b) 15 seconds treatment with 5 seconds step
2.3 Temperature monitoring

An estimation of the temperature of the discharge was given by indirect measurements in the outer walls of the DBDs (dielectric, electrode, oil and duct tape were in between the discharge and the measurement), using a K-type thermocouple. The oil was used in order for air not to exist between the electrode and the dielectric, which could result to a systematic loss of power. In order to find a relation between the measurement and the discharge, the heat diffusion equation is used:

\[ \frac{\partial T}{\partial t} = \kappa \nabla^2 T + f \]  \hspace{1cm} (2.3.0.1)

where \( \kappa \) is a positive constant and \( f \) is the heat rate input. Because we are interested only in the heat transmission in one dimension, equation 2.3.0.1 takes the form:

\[ \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + f \]  \hspace{1cm} (2.3.0.2)

Now we are going to show that for isotropic materials that are in contact, the derivative of temperature over time for the outer material is proportional to the respective derivative for the inner material.

\[ \frac{\partial T}{\partial t}\bigg|_{x=0}^{t=\tau} = \kappa \frac{\partial^2 T}{\partial x^2}\bigg|_{x=0}^{t=\tau} + f(\tau, 0) \]  \hspace{1cm} (2.3.0.3a)

\[ \frac{\partial T}{\partial t}\bigg|_{x=L_1}^{t=\tau} = \kappa \frac{\partial^2 T}{\partial x^2}\bigg|_{x=L_1}^{t=\tau} + f(\tau, L_1) \]  \hspace{1cm} (2.3.0.3b)

By dividing by members the above equations, we obtain:

\[ \dot{T}(\tau; L_1) = \alpha \dot{T}(\tau; 0) \]  \hspace{1cm} (2.3.0.3c)

By demanding the continuity of the derivative at the contact of the two materials:

\[ \dot{T}_1(\tau; L_1) = \dot{T}_2(\tau; L_1) \]  \hspace{1cm} (2.3.0.3d)

With the same procedure we obtain:

\[ \dot{T}_2(\tau; L_2) = \alpha_2 \dot{T}_2(\tau; L_1) = \alpha_2 \dot{T}_1(\tau; L_1) = \alpha_1 \alpha_2 \dot{T}_1(\tau; 0) \]  \hspace{1cm} (2.3.0.3e)

So by generalizing for \( N \) isotropic materials between the area of interest and the area of measurement, we find the proportionality relation:

\[ \dot{T}_{\text{Meas}} \propto \dot{T}_{\text{Discharge}} \]  \hspace{1cm} (2.3.0.4)
The temperature measurements and their derivatives over time for both dielectrics are shown in the graphs below.

![Graph](image_url)

(a) Measurements of Temperature - Time.

(b) Derivative of Temperature - Time

Figure 2.19: Results of temperature monitoring for the SiO$_2$ DBD. At 600 seconds the discharge is turned off and the cooling of the DBD can be observed.
2.3. Temperature monitoring

(a) Measurements of Temperature - Time

(b) Derivative of Temperature - Time

Figure 2.20: Results of temperature monitoring for the Al$_2$O$_3$ DBD

The above graphs give an estimation of temperature of the discharge, but only the derivative can be correlated as shown above.
2.4 Optical Emission Spectroscopy

For the identification of the plasma gas, optical emission spectroscopy was performed. The experimental setup consisted of a TRIAX 550 monochromator\textsuperscript{12} and the Symphony 1024 x 256 Thermoelectric Open Electrode CCD Detector\textsuperscript{13} manufactured by HORIBA. From the obtained spectrum, seven bands were able to be related to N\textsubscript{2} species and specifically to the second positive system of N\textsubscript{2} (C\textsuperscript{3}Π\textsubscript{u} → B\textsuperscript{3}Π\textsubscript{g}(1,0)) , using as reference the following table:

Table 2.5: Spectral bands of the N\textsubscript{2} species identified after comparison with literature. 

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Relative intensity (%)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Literature SiO\textsubscript{2} Al\textsubscript{2}O\textsubscript{3}</td>
<td>Literature SiO\textsubscript{2} Al\textsubscript{2}O\textsubscript{3}</td>
<td></td>
</tr>
<tr>
<td>313.6</td>
<td>314.5 314.1</td>
<td>2</td>
</tr>
<tr>
<td>315.9</td>
<td>316.8 316.4</td>
<td>5</td>
</tr>
<tr>
<td>333.9</td>
<td>334.3 333.9</td>
<td>0.3</td>
</tr>
<tr>
<td>337.1</td>
<td>337.4 337.1</td>
<td>19</td>
</tr>
<tr>
<td>353.6</td>
<td>353.4 353.1</td>
<td>3</td>
</tr>
<tr>
<td>357.6</td>
<td>359.4 359.1</td>
<td>9</td>
</tr>
<tr>
<td>375.5</td>
<td>377.0 376.6</td>
<td>3</td>
</tr>
<tr>
<td>380.4</td>
<td>381.9 381.5</td>
<td>5</td>
</tr>
<tr>
<td>399.8</td>
<td>400.8 400.4</td>
<td>1.5</td>
</tr>
<tr>
<td>405.9</td>
<td>406.7 406.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 2.21: OES spectra a) for the glass DBD, b) for the ceramic DBD

2.4. Optical Emission Spectroscopy

Furthermore, high resolution spectra (Fig. 2.22a and 2.22b) were obtained for both of the dielectrics which allow an estimation of the temperature using Boltzmann plots (Fig. 2.22c and 2.22d). This is accomplished by measuring the rotational lines of the 337.1 nm head, which correspond to the rotational energy separation. From the pyrometric line (the linear fit), the temperature can be calculated using equation 2.4.0.1.

\[
T_R = -\frac{hcB_e}{k_B \text{slope}}
\]  

(2.4.0.1)

In the literature\textsuperscript{14} the rotational constant \(B_e\) has the value of 2.01 cm\(^{-1}\) for the \(\text{N}_2\) molecule. Therefore, from the slopes calculated, the final approximate temperatures are respectively for the \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\) DBDs:

\[
T_{\text{Glass}} = 104 \ ^\circ\text{C}, \quad T_{\text{Ceramic}} = 234 \ ^\circ\text{C}
\]  

(2.4.0.2)

\textsuperscript{14}Atoms, Molecules and Photons, Wolfgang Demtröder, Springer-Verlag Berlin Heidelberg 2010, https://doi.org/10.1007/978-3-642-10298-1
2.5 FTIR analysis of the air around the DBD

For the identification of some of the species created during the discharge, FTIR spectroscopy was used. For that purpose, a vacuum cell was connected through a small tube in the space around the discharge and left to be filled with air from the immediate surroundings of the DBD device while it was active. The windows of the cell were from KBr and the spectrograph was functioning in transmittance mode with a resolution of 4 cm\(^{-1}\). From the resulting spectra, O\(_3\) and N\(_2\)O were identified. In Fig. 2.23, two peaks at 1054 and 1024 cm\(^{-1}\) were associated to the reference spectrum from NIST (1058 and 1029 cm\(^{-1}\) respectively). In Fig. 2.24, the peaks at 2236 and 2211 cm\(^{-1}\) were associated to the reference spectrum (2239 and 2208 cm\(^{-1}\) respectively).

![Figure 2.23](image)

Figure 2.23: a) FTIR spectrum (Transmittance %) of the air produced by the glass DBD and the small signal attributed to the existence of O\(_3\). Quasiclosed, fans on, Background: Air without the cell. b) FTIR spectrum of O\(_3\). Source: NIST Chemistry WebBook, Digitized by COBLENTZ SOCIETY
2.5. **FTIR analysis of the air around the DBD**

Figure 2.24: a) Gas produced by the ceramic DBD. Marked are the lines attributed to N$_2$O. Quasiclosed, fans off, Background: Vacuum. b) FTIR spectrum of N$_2$O. Source: NIST Chemistry WebBook, Digitized by COBLENTZ SOCIETY (BATCH I)

In the above, quasiclosed means that the discharge was covered by the bucket, and the background refers to the measurement in infrared. The species identified are one of the main reactive species, responsible for the plasma decontamination properties. Ozone is an oxidizing agent, and so is N$_2$O at elevated temperatures.
2.6 Current and light diagnostics

For both of the devices, current and light measurements were performed. The voltage source was a neon transformer which uses a Variac in order to convert the voltage of the network (220 Volts, 50 Hertz) with output characteristics of kV amplitude, maximum current of 20 mamps, sinusoidal signal with the frequency of the network. Every voltage value mentioned is from peak to peak. For the current measurements, one of the cables connected to the source was passed through a current monitor (PEARSON CURRENT MONITOR 6585\textsuperscript{15}) with a 1:1 Volt:Ampere ratio. For the light measurements, an optical fiber of the type QP-200-2-SR/BX from OCEANOPTICS\textsuperscript{16} (length = 1 m, fiber core size = 400 $\mu$m) was positioned in front of the discharge in a distance of about 1 cm (Fig. 2.25) and the whole setup was covered with a black cloth to avoid any stray light. The signal from the fiber was lead to a reverse biased LED (white LED, spectral response from 380-780 nm, peak at 450 nm) circuit (see Fig. 2.1 in the first section) and the voltage drop on the resistor of 7 $k\Omega$ as well as the current monitor signal were lead to a Tektronix TDS 5034B and the waveforms were saved in .TXT files. For voltages between 1.5 kV and 3.5 kV for the glass DBD and between 1.5 kV and 5.5 kV for the ceramic DBD, with 0.5 kV step, for both emitted light and current, three waveforms were obtained, one containing multiple surges, one containing a single surge, and one ”zoomed” containing a fraction of the pulses in a surge, resulting in a total of 84 waveforms. From these, the following results were obtained, namely the average intensity of the current spikes, the standard deviation and their number and the periods of surges and pulses as functions of the input voltage. The output files from the oscilloscope resulted in waveforms as they appear in the following pages.

Specifically for voltages of 1.5, 2.5 and 5.5 for the ceramic DBD and for 1.5, 2 and 3 kV for the glass DBD:

1. In Fig. 2.26 the surges of the ceramic DBD.
2. In Fig. 2.27 the surges of the glass DBD.
3. In Fig. 2.28 one surge of the ceramic DBD.
4. In Fig. 2.29 one surge of the glass DBD.
5. In Fig. 2.30 pulses (groups of spikes) of the ceramic DBD.
6. In Fig. 2.31 pulses of the glass DBD.

Waveforms of 1 and 2 were used for the calculation of time duration of the surges, the time difference between them and their period. Those of 3 and 4 were used to calculate the number of spikes in a surge, average intensity and standard deviation. Finally, the waveforms of 5 and 6 were used for the calculation of the pulse periods. The

\textsuperscript{15}http://pearsonelectronics.com/pdf/6585.pdf
\textsuperscript{16}https://oceanoptics.com/product/premium-grade-patch-cords/
waveforms in the graphs below are indicative and consist of the minimum, maximum and an intermediate "threshold" voltage. It should also be mentioned that the negative values of light in every waveform do not have any physical meaning and appear most probably due to electronic oscillations of the LED circuit.

Figure 2.25: Setup used for the emitted light measurements. The fiber was lead to an oscilloscope (not visible in the image)
Figure 2.26: Multiple surge graphs of current and light of the ceramic DBD for voltages of 1.5, 2.5 and 5.5 kV$_{P-P}$
Figure 2.27: Multiple surge graphs of current and light of the glass DBD for voltages of 1.5, 2 and 3 kV<sub>P-P</sub>
Figure 2.28: Single surge graphs of current and light of the ceramic DBD for voltages of 1.5, 2.5 and 5.5 kV_{P-P}.
2.6. Current and light diagnostics

Figure 2.29: Single surge graphs of current and light of the glass DBD for voltages of 1.5, 2 and 3 kV<sub>P-P</sub>
Figure 2.30: Pulses graphs of current and light of the ceramic DBD for voltages of 1.5, 2.5 and 5.5 kV<sub>P-P</sub>
2.6. Current and light diagnostics

Figure 2.31: Pulses graphs of current and light of the glass DBD for voltages of 1.5, 2 and 3 kV<sub>P-P</sub>
2.6.1 Number of current spikes contained in a single surge

In the tables below is shown the number of spikes that were counted in a single surge and whose absolute values were larger than 0.05 Amps, as this was the threshold set in order to filter out the noise of the oscilloscope. Their errors were calculated as the square root of their number, as every single spike was considered a stochastic process; these errors do not appear in the table because of their very small relative value.

Table 2.6: Number of positive and negative current spikes counted in the ceramic DBD

<table>
<thead>
<tr>
<th>Voltage (kV P-P)</th>
<th>Pos. Spikes</th>
<th>Neg. Spikes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>6869</td>
<td>7661</td>
</tr>
<tr>
<td>2.0</td>
<td>7179</td>
<td>8049</td>
</tr>
<tr>
<td>2.5</td>
<td>23374</td>
<td>26175</td>
</tr>
<tr>
<td>3.0</td>
<td>35327</td>
<td>40056</td>
</tr>
<tr>
<td>3.5</td>
<td>44935</td>
<td>51060</td>
</tr>
<tr>
<td>4.0</td>
<td>55799</td>
<td>63985</td>
</tr>
<tr>
<td>4.5</td>
<td>32378</td>
<td>38089</td>
</tr>
<tr>
<td>5.0</td>
<td>35447</td>
<td>42311</td>
</tr>
<tr>
<td>5.5</td>
<td>38771</td>
<td>48461</td>
</tr>
</tbody>
</table>

Table 2.7: Number of positive and negative current spikes counted in the glass DBD

<table>
<thead>
<tr>
<th>Voltage (kV P-P)</th>
<th>Pos. Spikes</th>
<th>Neg. Spikes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1066</td>
<td>1715</td>
</tr>
<tr>
<td>2.0</td>
<td>5782</td>
<td>7462</td>
</tr>
<tr>
<td>2.5</td>
<td>8379</td>
<td>10442</td>
</tr>
<tr>
<td>3.0</td>
<td>13808</td>
<td>16831</td>
</tr>
<tr>
<td>3.5</td>
<td>18786</td>
<td>22501</td>
</tr>
</tbody>
</table>

In Fig. 2.32, the above values are shown.
2.6. Current and light diagnostics

Figure 2.32: The number of positive and negative spikes in a single wavepacket (surge) for the two dielectrics and as a function of the applied voltage (P-P)

From the above graphs it can be seen that the number of negative and positive spikes is not equal. This is most probably due to the DBD mechanisms and surface charging during the secondary breakdown. The counts with a threshold of 0.04 Volts, results to an even larger asymmetry, leading to the hypothesis that a greater threshold (probably 0.06 Volts or more), would result in the same counts for positive and negative spikes. In any case, their trends appear to be the same.
2.6.2 Period of current and light surges

The resulting graphs from the multiple surge waveforms, provide time information about the period and duration of the surges. These graphs appear in Fig. 2.33.

(a) Ceramic DBD current surges
(b) Ceramic DBD light surges
(c) Glass DBD current surges
(d) Glass DBD light surges

Figure 2.33: Time information about the duration, period and difference between surges of current and light, for the two DBDs and as a function of the applied voltage (P-P)

From these results, it is observed that the light surges have a slightly greater duration than the respective current surges for the same voltage. It is also observed that for the values of 3 kVolts for the glass dielectric and 2.5 kVolts for the ceramic, the frequency with which the surges appear, is equal to 100 Hz which coincides with twice the frequency of the electrical network in Romania. The above values could be viewed as the minimum threshold of proper function of the discharge, therefore making valuable this particular diagnostics. The rest of the measurements could serve as a reference in order for the
voltage and thus the power, to be modified according to the specific substrate material and treated substance requirements.

2.6.3 Period of current and light pulses

From the zoomed waveforms in Fig. 2.30 and 2.31, the periods of the pulses were calculated. Since the spike groups or pulses seem to be superpositioned on triangular waveforms, the periods were calculated according to the first spike of the first group and the first spike of the last group in order to obtain the minimum possible error. It is mentioned that every period of the current corresponds to two periods of light emission since light is emitted for both positive and negative current. The resulting graphs appear in Fig. 2.34.

![Graphs showing periods of current and light pulses](image)

Figure 2.34: Periods of the current and light pulses as functions of the voltage (P-P)

a) Ceramic DBD, b) Glass DBD

It appears that after the aforementioned working voltage is reached, the period of the pulses stabilizes around 35-36 $\mu$s or 27.8 kHz. This frequency can be assigned to the filament life which is the channel of the current conveyance. If both positive and negative filaments are taken into account, then the frequency is equal to 55.6 kHz and equal to the frequency of the light pulses. We can conclude that the filaments appear with the above frequency of 55.6 kHz, which are detected as current and light, in a surge that appears with a frequency of 100 Hz, and the above are valid from the threshold voltages and more. The final number of filaments per second is given by:

$$f_{fil} = 55.6 \text{ kHz} \cdot 100 \text{ Hz} \cdot \text{Surge time duration} \quad (2.6.3.1)$$

The above equation consists a more proper criterion in order to find the number of filaments in a discharge than the simple enumeration that was performed in Section 2.6.1. and referred to the spikes irrelevance if for a pulse more spikes were registered.
2.6.4 Average intensity of the spikes

The last information about current, refers to the average intensity and standard deviation of the spikes. For this purpose, the single surge files were used as an input for the code in Labview, which is presented in the next section. The threshold of value registering was set to ±0.05 Volts (without this value included) which was the noise zone of the oscilloscope and for the two dielectrics, the results appear in Fig. 2.35 and the following tables.

![Figure 2.35: Average intensity of the current as a function of the applied voltage](image)

Table 2.8: Positive and negative current spikes averages and standard deviations for the ceramic DBD (Values of intensity in Amperes)

<table>
<thead>
<tr>
<th>Voltage (kV_P-P)</th>
<th>Pos. Avg. Intensity</th>
<th>Pos. STDV</th>
<th>Neg. Avg. Intensity</th>
<th>Neg. STDV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.10745</td>
<td>0.05489</td>
<td>0.10827</td>
<td>0.05715</td>
</tr>
<tr>
<td>2.0</td>
<td>0.11679</td>
<td>0.06954</td>
<td>0.11729</td>
<td>0.07015</td>
</tr>
<tr>
<td>2.5</td>
<td>0.10833</td>
<td>0.05911</td>
<td>0.10928</td>
<td>0.06192</td>
</tr>
<tr>
<td>3.0</td>
<td>0.10371</td>
<td>0.05293</td>
<td>0.10453</td>
<td>0.05411</td>
</tr>
<tr>
<td>3.5</td>
<td>0.10084</td>
<td>0.05004</td>
<td>0.10211</td>
<td>0.05143</td>
</tr>
<tr>
<td>4.0</td>
<td>0.09806</td>
<td>0.04703</td>
<td>0.10007</td>
<td>0.05030</td>
</tr>
<tr>
<td>4.5</td>
<td>0.09710</td>
<td>0.04770</td>
<td>0.09852</td>
<td>0.04985</td>
</tr>
<tr>
<td>5.0</td>
<td>0.09603</td>
<td>0.04675</td>
<td>0.09718</td>
<td>0.04864</td>
</tr>
<tr>
<td>5.5</td>
<td>0.09490</td>
<td>0.04912</td>
<td>0.09323</td>
<td>0.04832</td>
</tr>
</tbody>
</table>

What is observed from the above, is that the average values, while taking into account
Table 2.9: Positive and negative current spikes averages and standard deviations for the glass DBD (Values of intensity in Amperes)

<table>
<thead>
<tr>
<th>Voltage (kV&lt;sub&gt;P-P&lt;/sub&gt;)</th>
<th>Pos. Avg. Intensity</th>
<th>Pos. STDV</th>
<th>Neg. Avg. Intensity</th>
<th>Neg. STDV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.08501</td>
<td>0.03297</td>
<td>0.08225</td>
<td>0.03576</td>
</tr>
<tr>
<td>2.0</td>
<td>0.12282</td>
<td>0.08667</td>
<td>0.11667</td>
<td>0.08938</td>
</tr>
<tr>
<td>2.5</td>
<td>0.11665</td>
<td>0.07753</td>
<td>0.11471</td>
<td>0.08090</td>
</tr>
<tr>
<td>3.0</td>
<td>0.12384</td>
<td>0.08927</td>
<td>0.12124</td>
<td>0.08746</td>
</tr>
<tr>
<td>3.5</td>
<td>0.12188</td>
<td>0.08455</td>
<td>0.12139</td>
<td>0.08599</td>
</tr>
</tbody>
</table>

their standard deviations, present a very good accordance.
2.7 Labview VIs

The following two VIs were used in order for the current average values to be calculated. The first VI changes the format of the data files to a form of $\text{NUMBER,NUMBER}$, from a form of fixed width which would be more suitable for character array manipulation in C, for example. It is a prerequisite for the second VI which gives the average and standard deviation values for the spike intensity of the current. The VIs are provided without documentation, just as a reference for the completeness of this thesis.

2.7.1 VI for the delimiter characters replacement

The following VI receives as input a folder path, and accesses every file specified by the number of iterations (28 in our case), changes the format of the numbers from: 

\[ s \frac{1.2345678e-001}{s} \frac{1.2345678e-001}{cr} \]

whereas one of the two spaces in the initial format is reserved for the - sign, but in the final format, one or two additional characters per line are added if there are negative numbers. This format is more suitable for Labview. Finally, the new files overwrite the old ones in the path folder. Below, the front and the block panel of the VI are shown.

![Front panel of the VI used to change the delimiters of the files saved from the oscilloscope](image)

Figure 2.36: Front panel of the VI used to change the delimiters of the files saved from the oscilloscope
2.7. Labview VIs

Figure 2.37: Block panel of the above VI (Part I)

Figure 2.38: Block panel of the above VI (Part II)
2.7.2 VI for the calculation of the spike intensity average values

Figure 2.39: Front Panel

Figure 2.40: Block Panel (Part I)
2.7. Labview VIs

Figure 2.41: Block Panel (Part II)

Figure 2.42: Block Panel (Part III)
2.8 Conclusions and discussion

In this thesis, we tried to find if the atmospheric dielectric barrier discharge has any removal and/or chemical transformation effects on organic substances deposited on glass substrates, with the purpose of medical device decontamination from remains of pathogenic proteins. The results from UV-VIS and FTIR spectroscopies lead to the conclusion that the active radicals and the UV photons created during the discharge are capable of producing the above effects. From optical emission spectroscopy, the temperatures for the glass and ceramic dielectrics were found equal to 104 °C and 234 °C, respectively, by considering that the rotational splitting of the 337.1 nm, approximately follows a Boltzmann distribution. The parameter of temperature has to be taken into consideration when treating sensitive materials, like polyethylene terephthalate (PET) plastics. A suggestion for this to be resolved, is to limit the frequency of the power supply (< 50 Hz) or to use an adequate duty cycle of the driving HV.

The advantage that the atmospheric DBD provides, is the possibility a treatment line, in contrast with the usual vacuum plasmas that are used and require special chambers and the creation of high vacuum, which is energy and time consuming.

Furthermore, with current and light measurements, threshold voltages that refer to packets of pulses (surges) of twice the network frequency, were identified for both of the dielectrics. The above characterization is deemed necessary for any practical applications, because it can be associated with the frequency of the pulses (corresponding to the filaments) and furthermore, by approximating the voltage, the power of the discharge can be estimated.

Some relevant studies could also include the aforementioned estimation of the power output of the discharge and the variation of its current and light characteristics as well as its temperature with the variation of the dielectric constant (which is equivalent to the use of different frequency or material) and the variation of the dielectric’s thickness. It should be expected that the power output would increase with the dielectric constant and decrease with the thickness of the dielectric, but a quantification of the above would provide valuable information for practical applications.

Another problem that should be addressed is the proper ozone evacuation from the immediate surroundings of the discharge, because it suppresses the discharge and, if the system is open to the operator, it also consists a potential health hazard.

As an overall conclusion, the atmospheric dielectric barrier discharge appears to have a very good potential for decontamination of medical surfaces, but further studies should be carried out to ensure the safety, cost-efficiency and material friendliness of its use.


[8] https://earthobservatory.nasa.gov/Features/OzoneWeBreathe/ozone_we_breathe3.php


[16] The Use of the Spectrometric Technique FTIR-ATR to Examine the Polymers Surface, Wieslawa Urbaniak-Domagala, http://dx.doi.org/10.5772/48143


[22] https://www.sigmaaldrich.com/catalog/product/sigma/h7379

[23] https://webbook.nist.gov/


[26] https://www.sigmaaldrich.com/catalog/product/sigma/27815


Software used:

- LibreOffice, https://www.libreoffice.org/
- QtiPlot, https://www.qtiplot.com/
- LaTeX, https://www.overleaf.com/