Atomic Nitrogen Decontamination System (ANDS)

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Abstract: The biological decontamination using atomic nitrogen has already been demonstrated on contaminated small surfaces. For the decontamination of larger surfaces, we propose here the use of "brushes" consisting of a flow of molecular nitrogen at atmospheric pressure containing nitrogen atoms. This method can be used for biological disinfection at large scale with no ecological risks, since all active substances by which atomic nitrogen has decontaminating effects (i.e. N, OH, O_3, O, NO, etc.) in different states of excitation, are natural species occurring in the atmosphere, and molecular nitrogen itself is of course not dangerous. For example, all these active species involved in the proposed system are also produced naturally during lightning. - While the method described here is not directly addressing Cyber Security (although it targets viruses), the subject is of global importance related to all aspects of security.
Keywords: virus; decontamination; disinfection; atmospheric pressure discharges; plasma-chemistry; atomic nitrogen; hydroxyl radical; ozone

INTRODUCTION

Many methods have been proposed to inactivate microorganisms using plasmas *[see e.g. Sakudo et al., 2019; Ijaz et al., 2016]*, and especially those based on atmospheric pressure discharges and remote exposure are numerous, because of the practical simplicity and thermo-sensitive medium preservation. 15 years ago, a nitrogen afterglow at atmospheric pressure has been demonstrated to transport active species over long distances in small diameter tubes, with a very efficient biocide effect *[Ganciu et al., 2004]*. In more detail, a discharge gas composed of either high purity nitrogen, or a mixture of nitrogen with some controlled ppm of oxygen, as presented in *[Pointu et al., 2008]*, have been used, and fundamental or excited states of atomic or molecular species of parent gases were monitored. In these studies, two types of microorganisms were used as targets for surface decontamination tests: *Escherichia coli* bacteria and *Bacillus stearothermophilus* spores.

The device under study (***Fig. 1***) appears to be efficient in the decontamination of the inner surface of tubes. A correlative study on medical catheters demonstrated no significant degradation of the polyurethane wall surface. The analysis of post discharge spectra (***Fig. 2***) allowed us the determination of the activated molecular nitrogen temperature of ~300K *[Ganciu et al., 2005]*.

In the present time, this atomic nitrogen decontamination system (ANDS) is a possible and urgent solution for large-scale disinfection of contaminated surfaces and volumes, at a very reasonable price, and without negative ecological side effects.

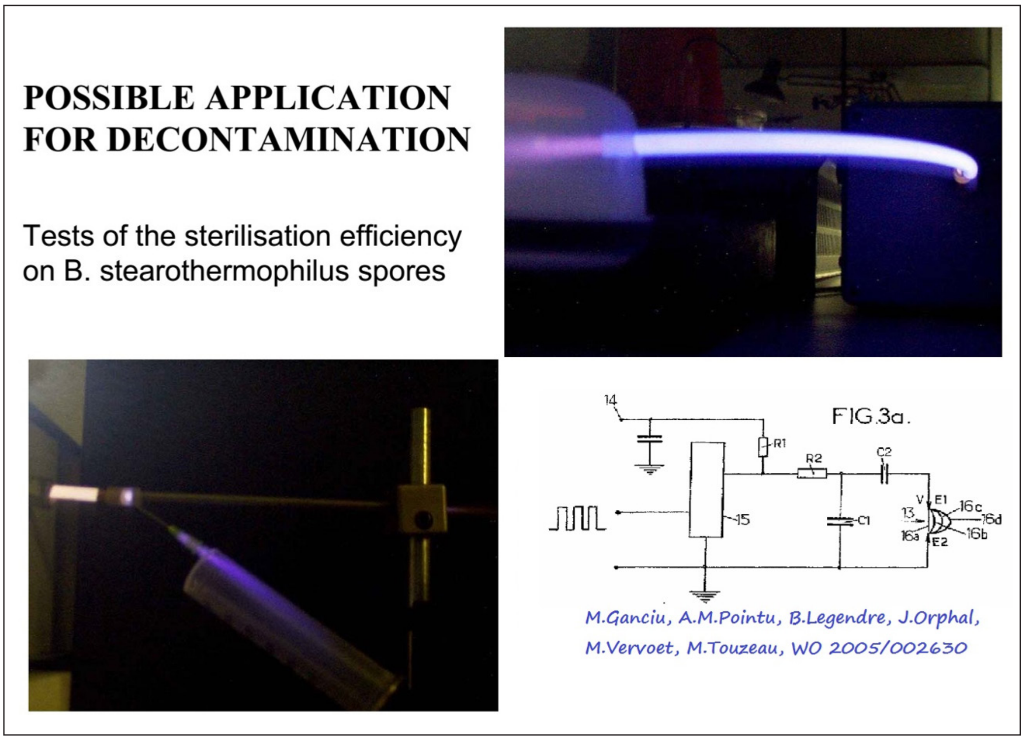

Fig. 1: *Decontamination of the inner surface of tubes using ANDS*

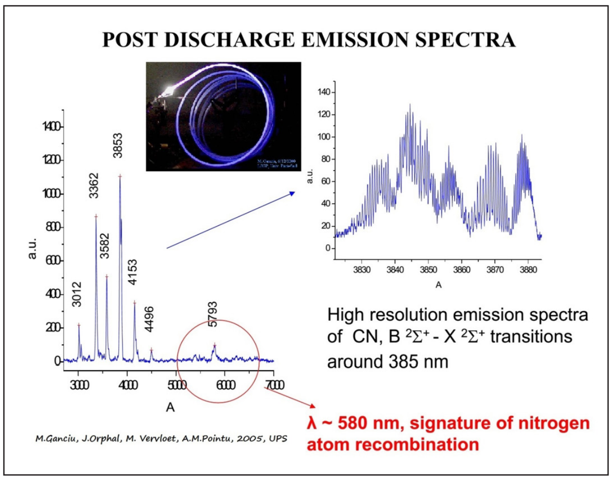

Fig. 2: *Analysis of the ANDS active flow by emission spectroscopy*

In particular, transport of chemically active species over long distances in ANDS was demonstrated. These species are not chemically or thermally aggressive to polymeric material, but have a proven biocide effect. Thus, ANDS is a feasible solution for large-scale decontamination.

The presence of nitrogen atoms at atmospheric pressure and temperature was proven using an original method, namely chemical titration with molecular oxygen *[Ganciu et al., 2005]*. The formation of oxygen atoms from the reaction between nitrogen atoms and molecular oxygen leads to the rapid production of ozone, which was quantified by its strong ultraviolet absorption. This titration, together with chemical simulations, also showed the high concentration of nitrogen atoms, about 10^{15} per cm^3, in the ANDS flow. This titration method is generally interesting for nitrogen atom diagnostics in decontamination or industrial processes at atmospheric pressure, particularly because of potential difficulties related to the classical method of NO titration used at lower pressures, for example to achieve a homogeneous mixture in the characteristic time of the reaction. Furthermore, using larger quantities of NO for titration is hazardous, because NO is a toxic and corrosive substance that is much more difficult to handle than molecular O_2.

ANDS METHODOLOGY AND PROJECT DESCRIPTION

Due to highly dangerous and rapidly evolving situations such as the present Coronavirus world-wide spread, it is important to preserve and develop the skills in the generation, transport and use of atomic nitrogen, with a much higher decontaminating effect than ozone and with the potential to penetrate into hard-to-reach areas. It is certainly a slightly more expensive process than the use of ozone, but has beneficial complementary effects *[Ganciu et al., 2004]*.

We believe that the most important channel of decontamination using atomic nitrogen is the formation of OH, following the N atoms' interaction with O_2 and H_2O from the microorganism's surface or very low amounts of O_2 and H_2O in the decontaminated zone.

The green (557.7 nm) emission emerging when small amounts of molecular oxygen are added to the nitrogen stream containing also atomic nitrogen is a clear evidence of the formation of the metastable oxygen, that leads to the dissociation of water molecules and to the formation of two OH molecules. A recent study *[Lee Jr. et al., 2018]* strongly endorses this hypothesis. In ***Fig. 2*** one can see clearly the signature of the pressure-enhanced "forbidden" transition of the $O(^1S)$-N_2 to $O(^1D)$-N_2 complexes (emission in green centred at 557.7 nm). These oxygen atoms are subsequently responsible for the formation of OH by the reaction $O(^1D) + H_2O \rightarrow 2\,OH$.

In ***Fig. 3a***, the discharge is in pure molecular nitrogen: the emission in blue is due to the fluorescence induced by the de-excitation of CN molecules from nitrogen organic impurities. In ***Fig. 3b***, the ANDS nitrogen flow with atomic nitrogen was conducted into a volume containing molecular oxygen, leading to the green emission explained above.

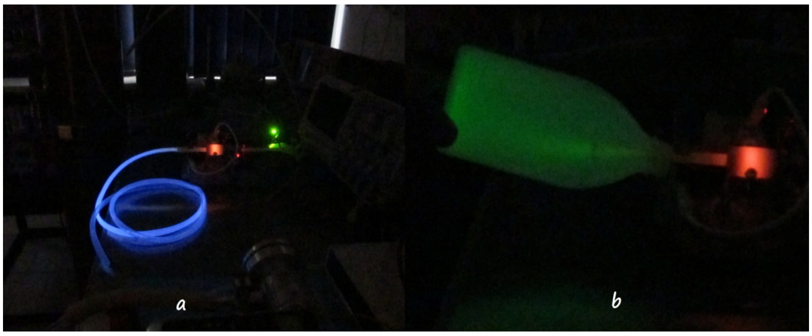

Fig. 3: (a) *ANDS using pure molecular nitrogen (the blue light is fluorescence induced by the de-excitation of CN molecules created on the inner surface of the tube);* ***(b)*** *ANDS using pure molecular nitrogen added to a volume containing O_2 (the green light emission is due to atomic oxygen created in the volume)*

The important role of OH for decontamination is described in much detail in a patent *[Hancock, 2018]*, so we summarize only the most important aspects here below:

1. OH radicals can be used to cause irreversible damage to cells and ultimately kill them;

2. The threshold potential for eliminating microorganisms is ten thousandths of the disinfectants used indoors and outdoors;

3. The biochemical reaction with OH is a free radical reaction and the biochemical reaction time for eliminating microorganisms is about one second, meeting the need for rapid elimination of microbial contamination, and the lethal time is about one thousandth of that for current disinfectants;

4. The lethal density of OH is about one thousandth of the spray density for other disinfectants - this will be helpful in eliminating microbial contamination efficiently and quickly in large spaces, e.g. bed-space areas;

5. Finally, the OH radicals or aerosols oxidize the microorganisms into CO_2, H_2O and micro-inorganic salts. The remaining OH will also decompose into H_2O and O_2, thus this method will eliminate microbial contamination without pollution.

Additional details about the physics involved in the ANDS are provided in our patent *[M. Ganciu et al, 2004]*. Here we provide hyperlinks to a few videos explaining the atomic nitrogen generation at atmospheric pressure and ambient temperature in molecular nitrogen flow.

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https://drive.google.com/file/d/1yklz8J1mLTg99fJeuMfXi4uRpAMdg7a-/view?usp=sharing

The first video shows the evolution of the discharge following the optimization of the gas flow and the second, synchronous with the first, the appearance of the specific lines of atomic nitrogen around 820 nm. ***Fig. 4*** shows an overview of the new Atomic Nitrogen Generator that is the basis of ANDS.

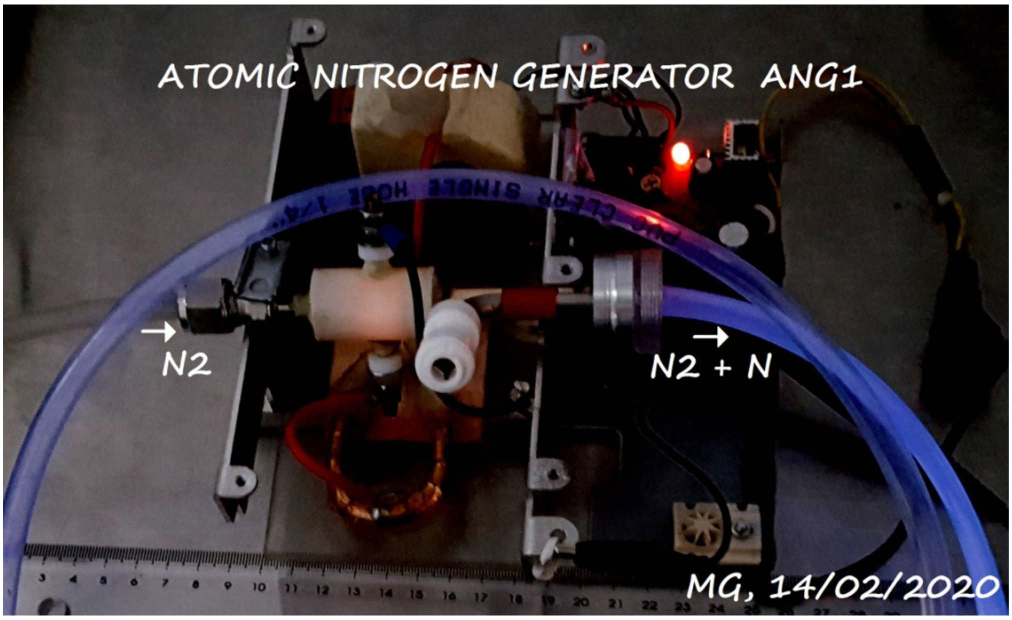

Fig. 4: *Overview of a new Atomic Nitrogen Generator*

Specific to the new Atomic Nitrogen Generator (ANG) are the discharge configuration and the applied electrical pulses, with amplitude, frequency and transferred charge which must be adapted to the gas flow. The performed studies were for a gas flow of 20-50 l/min at atmospheric pressure and a temperature of ~300 K. Additional details are given in our patent *[Ganciu et al., 2004]*.

At least the discharge tube structure may be realised by RAPID 3D structure printing. All the electronics can be compacted and only the high voltage transformer should be produced by a specialized company. The gas distribution part, in different geometries, adapted to the applications envisaged, can also take advantage of 3D printing. Thus, production of the ANG in large quantities for large-scale application of ANDS is possible.

A discharge spectrum emitted between the two point electrodes of an ANG under optimal discharge conditions is given in ***Fig. 5***. A comparison is made with the spectrum of a dielectric-barrier discharge (DBD) using the same electrical pulse generator.

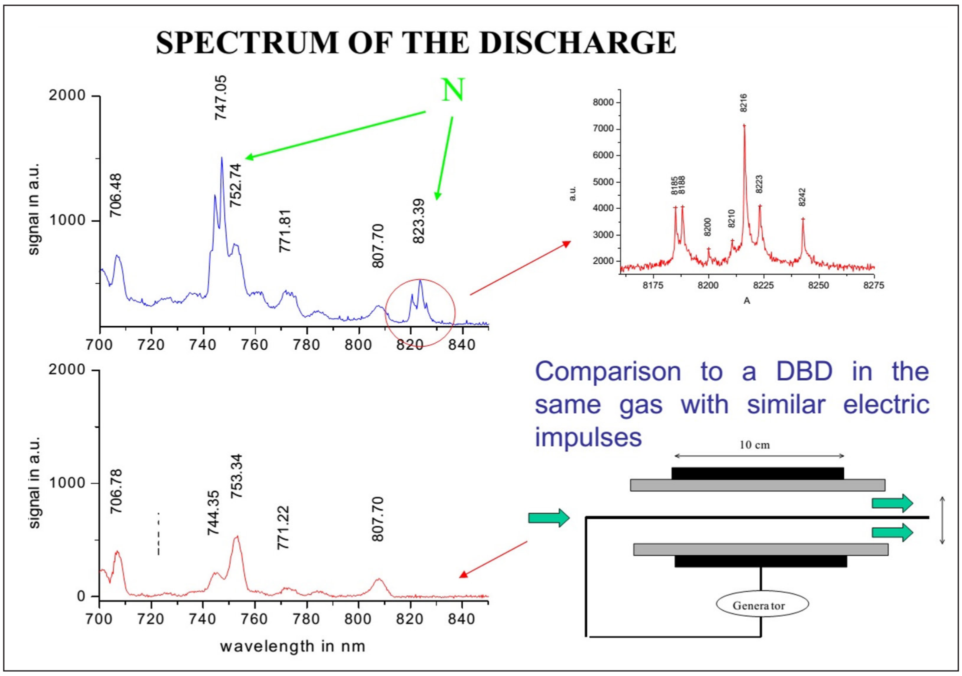

Fig. 5: *Discharge spectrum emitted between the two point electrodes of an ANG under optimal discharge conditions; comparison with the spectrum of a dielectric-barrier discharge (DBD) using the same electrical pulse generator*

Some aspects of the physico-chemical processes involved in the use of atomic nitrogen for decontamination can be found in *[Pointu et al., 2008]*. The viral disinfection effect of nitrogen plasma was analysed in *[Sakudo et al., 2016]*.

However, until now, the reaction channel involving OH production from the $O(^1D) + H_2O$ -> 2 OH reaction was missing, which we now consider to be very important in the decontamination, especially since the OH is created locally at exactly those places where the OH radicals are useful for decontamination.

Previously, the decontamination by atomic nitrogen was tested on contaminated small surfaces *[Pointu et al., 2008]*. For the decontamination of larger surfaces using ANDS, we now propose the use of “brushes” with atomic nitrogen. We believe that it can also be used for hand disinfection, since the active substances by which atomic nitrogen has a decontaminating effect (N, OH, O_3, O, NO) in different states of excitation are natural and molecular nitrogen is not toxic. In addition, nitrogen can be easily stored as a non-flammable gas. We have actually tested this application of ANDS ourselves on our hands, and no chemical or biological damage was observed, neither directly or long-term.

Note that all the active species involved in ANDS are also produced naturally during a lightning storm, like the one shown in ***Fig. 6***. So, what we are actually doing in ANDS is to reproduce part of the effects due to lightning - but at the right place and in the right proportion. The active species produced when applying this method are actually in very small quantities when compared to what results from a lightning during a storm. However, lightings do not produce them at those locations, where these species can be useful in fighting e.g. the Coronavirus through a complementary disinfection method.

Fig. 6: *Lightning storm. (Credit Shutterstock - 288803276)*

CONCLUSIONS

1. Atomic nitrogen has an antiviral effect and can be used at least for air conditioning decontamination and for closed areas. Atomic nitrogen is transported by molecular nitrogen and can enter areas where disinfectants in solution do not reach. The active species with decontaminant role (N, OH, NO, O, O_3, etc.) are produced following the plasma-chemical reactions induced by the atomic nitrogen where it arrives, that is *in-situ*.

2. At least on cruise ships, trains, buses, subways and elevators, the use of additional disinfection with atomic nitrogen would reduce the spread of viruses.

3. The atomic nitrogen based decontamination method ANDS can provide complementary disinfection that slows the spread of viruses, thus saving time until the weather warms up, and the spread of viruses is inhibited.

4. The viral disinfection by ozone has been used for over 50 years, but it also has many drawbacks related to a relatively long life of ozone and, to be effective on viruses, significant quantities are necessary making it toxic to humans too. An area disinfected with ozone must be subsequently aerated for over an hour. The validation of viral disinfection by ozone implies also the validation of viral disinfection by using atomic nitrogen in molecular nitrogen flux.

5. Ozone is the final compound after atomic nitrogen generates other compounds much more active than ozone. If oxygen is used instead of nitrogen, ozone is obtained directly. If needed, only compressed air can be used which leads mainly to ozone generation but also to nitrogen oxides which should be rather avoided.

6. A demonstration of great effect would be the disinfection of an airplane. One can start with a smaller one, it would take about a bottle of nitrogen. One can also think of a generator adapted for this application. It would be the nitrogen bottle, and a hose finished with a cylinder with a volume of 2 litres (high power Atomic Nitrogen Generator).

7. A robotic system that transports the atomic nitrogen generator together with the associated nitrogen cylinder would be very useful at least inside airplanes. Activated nitrogen must be released near the decontaminated areas (it reacts with residual O_2 and H_2O) or the aircraft must first be filled with molecular nitrogen and then atomic nitrogen is introduced. This will reduce the amount of ozone that has a rather long life.

8. It can be made even simpler by using atomic nitrogen from the beginning during few minutes, after which the plane is aerated for several hours to remove ozone (ozone is also good for disinfection).

9. We want to specify that the ANDS method may not be the solution to “everything” but it can be complementary to other methods, increasing the sterilization efficiency. However, the gaseous effluents also penetrate the hidden places, in contrast to other methods.

10. At least the discharge tube structure could be realised by RAPID 3D structure printing. All the electronics can be compacted, and only the high voltage transformer will be produced by a specialized company. Thus, large-scale production of ANDS is possible.

11. The gas distribution part, in different geometries, adapted to the applications envisaged, can also take advantage of a 3D printing.

CONFLICTS OF INTEREST

The authors declare no conflict of interest. The funders had no role in the design of the study, in the collections, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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