Chapter 26

Air Purification Technology by Means of Cluster Ions Generated by Plasma Discharge at Atmospheric Pressure

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Abstract The increased density of our living environment coupled with pollution of the atmosphere has led to a growing need for the removal of harmful molecules in the air (1). As a result research into applying a plasma discharge into the atmosphere and creating ozone and radicals of strong chemical reactivity to purify the air environment has gathered momentum. The removal of airborne particles, such as bacteria, allow for an improvement in indoor air quality so that our environment is healthy and pleasant. Within the medical field, illnesses caused by viruses such as influenza and SARS (2), hospital infections caused by airborne bacteria, fungi and allergic bronchial tube asthma (3), Japanese cedar hay fever caused by inhaling cedar pollen (4) are becoming large social concerns.

In this research article, we discuss how we have applied our novel plasma discharge technology to produce positive and negative "cluster" ions. This ion-generating device operates at a normal atmospheric pressure. Subsequent investigations have permitted characterization of the resultant cluster ions. We have performed a series of experiments to prove the air purification effects of cluster ions, paying close attention to airborne harmful microbes and cedar pollen allergens.

26.1 Ion Generating Device

An electrode is formed on the surface of the flat ceramic dielectric body. This ceramic body is attached to high voltage and applied electrodes. The high AC voltage is applied permitting a plasma discharge state on the surface. If molecular energy from the air is applied by plasma discharge, ionization and dissociation of the airborne molecules occurs. These events all occur at atmospheric pressure (5).

The ion generating device has been designed to allow the discharged electron energy to become a monochrome beam. When the optimal 5 eV voltage is applied each molecule in the atmosphere there is distribution from the electrode.

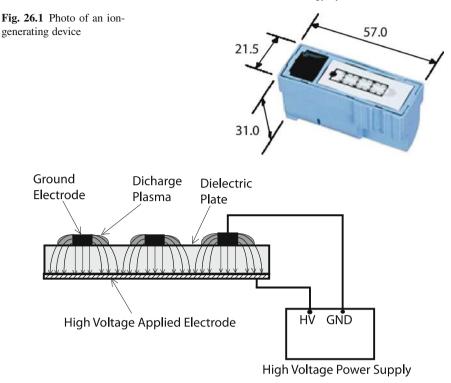


Fig. 26.2 Section diagram of an ion-generating electrode

The concentration of ozone has been confirmed to be less that 0.005 ppm in the vicinity of the device. This value has been deemed safe by a number of health bodies over the world including the Association of Home Appliance Manufacturers, AHAM. We always measure this since there have been numerous reports of the differences in concentration of Ozone from ion-generating devices.

This device is displayed in Fig. 26.1 and shows the actual component used in many SHARP products. In Fig. 26.2, the ion-generating device is shown in cross section and highlights some of the points stated above.

26.2 Characteristics of Positive and Negative Ions

The ion density is measured using an air ion counter (Dan Science 83-1011B) (7) by means of the double concentric circle tube method (6).

For identification of the type of ion we measured the mass spectrum of the positive and negative ions (Fig. 26.3a and b) using a flight time decomposition analysis apparatus. For the positive ions oxonium ions $\rm H_3O^+$ were generated and around them, cluster ions of $\rm H_3O^+(H_2O)_m$ with a structure of water molecules aligned

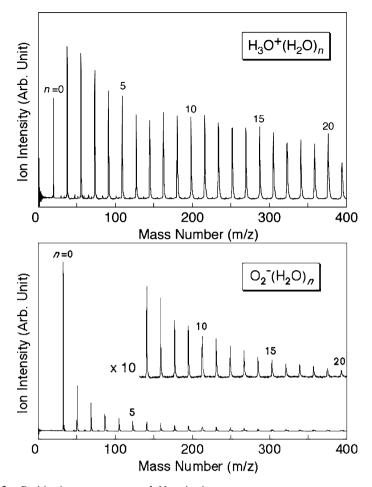


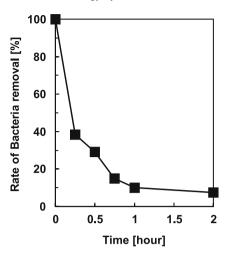
Fig. 26.3 a Positive ion mass spectrum. b Negative ion mass spectrum

($_{m}$ is constant), for the negative ions, oxygen molecule ions O_{2} were generated and around them were cluster ions of $O_{2}^{-}(H_{2}O)_{n}$ with a structure of water molecules aligned around them ($_{n}$ is constant). Other types of ion generation were not found during our studies.

26.3 Effect of Removing Airborne Bacteria

Bacillus coli cultures were sprayed as a mist into a room with a volume of 30 m. Measurements was made to calculate the density of bacillus coli using an air sampler. The results are shown in Fig. 26.4 and display the changes with the passage of time of the amount of bacillus coli in the air. The effect of removing 90% of *bacillus*

Fig. 26.4 Effect of removing bacillus coli in air by positive and negative cluster ions; *Y* axis = Rate of Bacteria removal; *X* axis = Time



coli in the air required one hour when discharging cluster ions at a mean ion density of 3000/cm³.

Figure 26.5 shows a photo of a Petri dish of the *bacillus coli* collected cultivated during 24 hours in LB agar medium. Without generating cluster ions, the growth of *bacillus coli* colonies was confirmed. When positive and negative ions were applied, the generation of colonies were not observed. This showed that the growth of *bacillus coli* is prevented resulting from their deactivated by positive and negative cluster ions.

Figure 26.6 shows changes with the passage of time in the density of the *bacillus coli* due to positive and negative ions. In the case of negative ions only (mean density 6000/cm³), the ratio of remaining bacteria after one hour was 85% (removal rate 15%), and the effect of removing bacteria was extremely small and even after more time passed, no more were removed. In contrast, in the case of positive and negative ions with added positive ions (mean density 3000/cm³), the ratio of re-

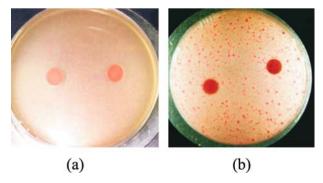
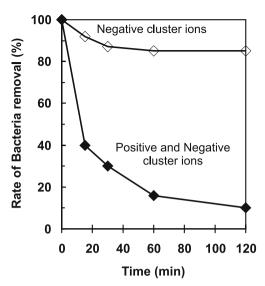


Fig. 26.5 Photo of bacillus coli incubation in a Petri dish a with ions and b without ions

Fig. 26.6 Characteristic of suspended *E. coli* bacteria removal with the positively and negatively charged ions, and the negatively charged ions



maining bacteria after one hour was 16% (removal rate 84%), and a large removal effect was obtained. From this we can see that a removal effect of bacteria can be achieved by positive and negative cluster ions.

MRSA (Methicillin-resistant Staphylococcus aureus) that is a common hospital acquired infection was sprayed into a box with a volume 1 m³. The density of MRSA in the air measured using an air sampler. Positive and negative cluster ions were discharged into the air (mean density 10,000 cm³) and it was found that after 30 minutes, 90% of the original MRSA concentration in the air had been removed and after 60 minutes no MRSA could be found in the air. Figure 26.7 shows the changes with time of the density of floating MRSA in the air.

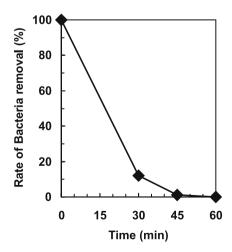


Fig. 26.7 Effect of removing MRSA (methicillin-resistance staphylococcus aureus) in air by positive and negative cluster ions

26.4 Effect of Removing Floating Fungi (Mould)

Cladosporium spores were sprayed into a box of 1 m³ and the density of floating fungi in the air measured. Figure 26.8 shows the changes with time in the density of the floating fungi in the air.

By discharging positive and negative cluster ions into the air (mean density $10,000/\text{cm}^3$), it was confirmed that 90% of the fungi were removed after 45 minutes and after 60 minutes more than 99%. Figure 26.9 shows the state of propagation of fungi when positive and negative ions and negative ions only were used. When left for 10 days, propagation of the fungi could be seen when there were only negative ions, but when there were positive and negative ions, the fungi were not found to propagate.

From this we observed that positive and negative cluster ions have the profound effect of restricting propagation of fungi.

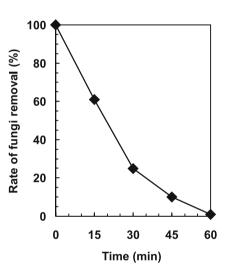


Fig. 26.8 Effect of removing fungi count (*cladosporium*) in air by positive and negative cluster ions

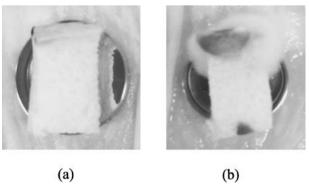


Fig. 26.9 Photographs of the mold growth with the operation of positively and negatively charged cluster ions (a), and negatively charged cluster ions (b)

26.5 Effect of Deactivating Floating Viruses

The apparatus used to test viruses required a slightly different set up and Fig. 26.10 shows a schematic example of this. The ion-generating device is installed in an acrylic tube of length 200 mm and an external diameter (only if the ion density is $2000/\text{cm}^3$) of 170 mm. At one end of the tube an atomizer is attached to spray the virus, while the other side required an impinger to collect the virus. In our extensive experiments, the influenza virus A(H1N1) A/PR8/34 was used. The atomizer contained 10 mL of virus solution and was attached to one end of the cylindrical test apparatus.

The impinger contained 10 mL of phosphate buffer solution (PBS). From an air compressor air supply, air at a of speed 4 m/s was passed into the cylinder (if the ion density if 2000/cm³ only the air speed is 0.4 m/s), the virus was sprayed and passed over the ion generating device within the cylinder. The volume of spray was 3.0 mL and the spray speed set at 0.1 mL/min. Taking the case of when the ion generating device is not being operated as the control, we compared the amount of virus when the ion generating device was operated. Tests were carried out with the ion density of positive and negative ions of 200,000 cm³, 100,000 cm³, 50,000 cm³ and 5000 cm³ and 2000 cm³. The air that passed through the tube was collected by the impinger for 30 minutes intervals at a sampling speed of 10 L/min.

The ion density was measured at a distance of 10 cm from the jet part of the cylinder test apparatus. The atmosphere was kept at a temperature of 18 ± 1 °C and relative humidity $43 \pm 2\%$.

Figure 26.11 shows the ratio of the number of formations of plaque of influenza depending on the ion density. The measurements used the plaque method which uses Madin-Darby canine kidney (MDCK) cells. Taking the number of plaques when the ion-generating device is not in action during the control as 100%, when the ion density of 200,000 cm³, 100,000 cm³, 50,000 cm³ and 5000 cm³ and 2000 cm³ is

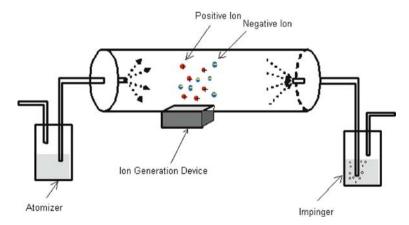
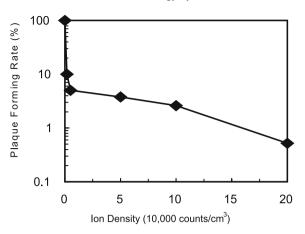


Fig. 26.10 Schematic diagram of the test apparatus

Fig. 26.11 Influenza virus plaque forming rate by the plaque method using MDCK cells



acted on by the influenza virus, a reduction of the number of plaques of 99.5%, 97%, 96%, 95% and 90% was found.

When this was the case the ozone density was less than 0.005 ppm. Also, the when the ion density was less than $100/\text{cm}^3$ and the ozone density 0.005 ppm, a reduction of the number of plaques was not found.

Figure 26.12 shows a photo of the MDCK cells that have been vaccinated with the influenza virus acted on by ions and not acted on by ions. When the influenza virus acted on by ions was vaccinated, the virus has been deactivated by the ions so the transmission to the cells could not be seen and the cells maintain their normal shape.

Figure 26.13 shows a photo of the red cell aggregation reaction of the influenza virus acted on by ions and not acted upon. It shows the properties that gather in the centre when red blood cells are placed in a receptacle that has a hollow in the centre (top photo). The red cells are aggregated by the protein on the surface of the virus when the influenza virus that has not been acted on by ions is vaccinated into the



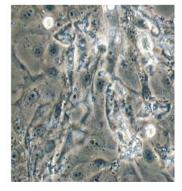


Fig. 26.12 Efficacy evaluation against influenza virus test of viral infection in madin-darby canine kidney (MDCK) cells

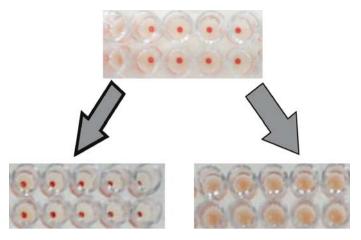


Fig. 26.13 Observation the mode of red blood corpuscle vaccinated with influenza virus

red blood cells, and the red blood cells no longer collect in the centre (bottom right photo). Even if the influenza virus that has been acted on by ions is vaccinated into the red cells, aggregation of the red blood cells due to the virus does not occur and the same properties as normal blood cells were shown (photo bottom left). When the ions are made to act on the influenza virus, it was found that the function of the protein that causes the aggregation reaction (hemagglutinin) and the red cells on the virus surface is reduced.

26.6 Virus Deactivation Model Using Cluster Ions

The effect of deactivating the influenza virus in the air with positive and negative cluster ions generated has been confirmed. Figure 26.14 shows the influenza deactivation model in the air due to positive and negative cluster ions. Further work has been carried out to define this method, however the results we not available for this manuscript. It is thought that the cluster ions collide with viruses in the air and surround the virus.

Positive cluster ions H_3O^+ ($H_2O)_m$ ($_m$ is constant) and negative cluster ions $O_2^-(H_2O)_n$ ($_n$ is constant) react on the surface of the virus and active species of very high reactivity are generated. Our future work will determine which surface molecules are indeed effected by these cluster ions. However we postulate that these cluster ions alter the protein of the virus surface. In the influenza virus, the protein hemagglutinin that protruded from the surface is altered by cluster ions (8). Hemagglutinin performs a key role in the assay permitting red blood cell (RBC) aggregation. As the hemagglutinin is altered by the ions, it is thought that the influenza virus is deactivated and little or no RBC aggregation was observed.

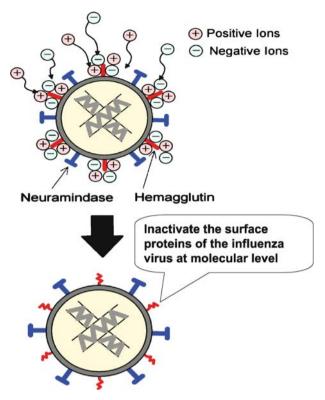


Fig. 26.14 Model for inactivation of infection capacity from viruses

26.7 Allergen Deactivation Effect

Crude antigens (protein density 200 ng/mL) extracted from Japanese Cedar pollen were sprayed in a mist using a nebulizer into the cylindrical receptacle of 0.9 L capacity. By operating an ion generating device placed in the receptacle, positive and negative cluster ions were generated in the receptacle space. The cedar pollen crude antigens exposed in cluster ions were collected for about 90 seconds. Following this 5 sets of analyses were performed: an allergen evaluation reaction, ELISA method, ELISA inhibition method, intradermal reaction and a conjunctival reaction tests.

26.7.1 Allergen Evaluation Reaction

The main antigens found in the cedar pollen are Cry j1, Cry j2. The presence of these proteins in the air determines the extent of reactivity with, for example, humans. The results of the evaluation by the ELISA method (Fig. 26.15) show the reactivity of

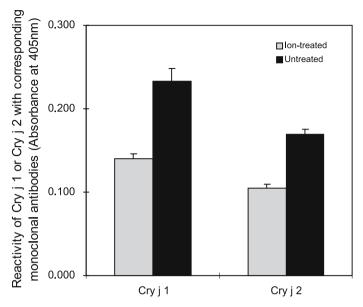


Fig. 26.15 The charged ions reduced the antigenicities of Cry j1 and Cry j2 with cedar pollen allergen

Cry j1, Cry j2. The assay concerns the reactivity of their respective monoclonal antibodies and as shown, their reactivity is reduced by the cluster ions.

26.7.2 ELISA Method

In both Cry j1 and Cryj2, the reactivity with the monoclonal antibodies reduced significantly. In particular the reduction of the reactivity of Cry j1 and its monoclonal antibodies was notable. The ELISA method evaluated whether the reaction between the cedar pollen crude antigens and the Immunoglobulin E (IgE) blood serum of the cedar pollen allergy sufferers changes due to the cluster ions. The results of evaluating the blood serum from 42 different sufferers showed that in 33 patients, due to the cluster ions, regarding the crude antigens, the reactivity with the blood serum IgE of patients reduced significantly. In 2 patients the reactivity with IgE reduced more than 80%, in 3 patients 70-80%, in 5 patients 60-70%, in 8 patients 50-60%, in 6 patients 40-50% and in the final 4 patients it reduced by 30-40%.

26.7.3 ELISA Inhibition Method

To evaluate quantitatively the allergy reaction deactivation rate of the cedar pollen crude antigens and the cedar pollen allergy sufferers' blood serum IgE by cluster ions, the ELISA inhibition method was carried out. The results of this assay can be seen in Fig. 26.16. When the antigenecity at inhibition rate 50% was evaluated, in cluster ion processing crude antigens 13.5 ng is required while in the case of crude antigens without processing 2.83 ng were required. The cluster ion processing antigens showed the same inhibition rate in an amount of about 4.8 so it was confirmed that the reactivity between the cedar pollen crude antigens and the patients' blood serum IgE was reduced by about 79% by the cluster ions.

26.7.4 Intradermal Reaction and Conjunctival Reaction Tests

We evaluated intradermally and by a conjunctival reaction test whether the allergenity of the cedar pollen crude antigens changes *in vivo* due to the effect of cluster ions.

For the intradermal reaction $0.02\,\mathrm{mL}$ of a diluted mixture of cedar pollen crude antigens and 0.9% solution of NaCl with a protein density of $0.5\,\mu\mathrm{g/mL}$ was injected into the skin of the forearm flexor side of the cedar allergy sufferer using a tuberculin hypodermic needle. The diameter and radius of the wheals and red spots that arose after about 15 minutes were measured and from these mean radii the reactivity was evaluated. We made red spots of less than $10\,\mathrm{mm}$ –, red spots of $10-20\,\mathrm{mm}$ ±, red spots of $20-30\,\mathrm{mm}$ and wheals of less than $10\,\mathrm{mm}$ +, red spots of $30-40\,\mathrm{mm}$, wheals of $10-14\,\mathrm{mm}$ ++, red spots of more than $40\,\mathrm{mm}$, wheals of more than $15\,\mathrm{mm}$ and things giving pseudopodia to the wheals +++. The results of

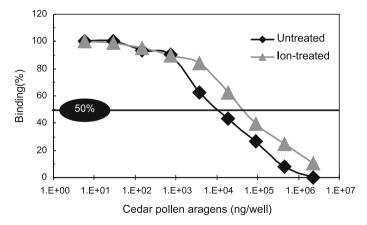


Fig. 26.16 Inhibition of IgE-binding to untreated Japanese cedar pollen allergen with various concentrations of ion-treated or untreated Japanese cedar pollen allergens

26.8 Conclusion 637

carrying out intradermal reaction exams on 6 cedar allergy sufferers showed that in all patients the intradermal reactivity due to cedar pollen crude antigens reduced from +++ to + due to cluster ions.

With respect to the conjunctival reaction, $5 \,\mu L$ of a mixture of cedar pollen crude antigens was diluted in 0.9% NaCl at a protein concentration of $0.5 \,\mu g/mL$ was dropped into the eyes of 6 cedar pollen sufferers using a pipette. In addition, the same test was performed with; however $5 \,\mu L$ of a mixture of cedar pollen crude antigens had been treated with cluster ions before mixing into solution with PBS.

Following incubation for 15 minutes, the extent of any conjunctival reaction was observed. This qualitative test covers a number of different areas which include: meniscus skin wall, the congestion of the eyelid skin and spherical conjunctiva, itchiness and tears. When no congestion was observed, we assessed it as 1, when there was slight congestion and itchiness \pm , when congestion was seen on either the lower or upper conjunctiva of the eyeball +, when congestion was seen on both the upper and lower eyeball conjunctiva ++, and when congestion was found on all the eyeball conjunctiva +++ and when edema of the eyelid was seen +++++.

Tests for the conjunctiva reaction were carried out on 6 cedar pollen sufferers and the results showed that in 5 patients the conjunctival reactivity due to cedar pollen antigens was reduced from ++ to - due to cluster ions and we understood that the potency of the conjunctiva reaction was lost.

26.8 Conclusion

We have developed an ion generating device for generating positive ions H_3O^+ and negative ions O_2^- . Also we have demonstrated the effect of removing pollen allergens and airborne harmful microbes (fungi, bacteria and viruses) as well as pollen allergens.

The air purification technology developed that uses positive and negative cluster ions shows many excellent characteristics for purification of the environment and it is expected that it will develop into a wide range of applications in industry types other than household products.

References

- Tetsuji Oda et al. (2000) The future of Technologies on Environmental Measures by Discharge. Japan Society of Applied Physics 69:263–289
- 2. Bunshichi Shimizu (1996) Understanding the Virus, Koudansha, pp 129-187
- Yoichi Minamishima, Yasuo Mizukuchi, Hiroaki Nakayama (1987) Current Microbiology, Nanzando
- 4. Yozo Saito et al. (1994) The Science of Hay fever
- Journal of The Japan Research Group of Electrical Discharges (1998) Discharge Handbook, Oum, pp 400–417
- Shinichiro Kitagawa, Zenichiro Kawasaki, Kazuhiko Miura, Koichiro Domoto (1996) Study of Atmosphere Electricity, Published by Tokai University, pp 45–61
- 7. Tadashi Akiyama (1997) Clean Technology 8:54–58
- Artmann et al. (2005) Bactericidal effects of plasma-generated cluster ions. Med Biol Eng Comput 43(6):800–807