

# Applications of Air Ionization for Control of VOCs and PM<sub>x</sub>

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**Dr. Stacy L. Daniels**

Director of Research, Precision Air, a Division of Quality Air of Midland, Inc.  
3600 Centennial Drive, Midland, MI 48642

## ABSTRACT

Recent developments in the application of controllable air ionization processes have led to significant reductions in airborne microbials, neutralization of odors, and reductions of specific volatile organic compounds (VOCs) in the indoor air environment. Removal of very fine particulates (PM<sub>x</sub>) by conventional HEPA filters also is enhanced by air ionization. The process of air ionization involves the electronically induced formation of small air ions, including superoxide O<sub>2</sub><sup>-</sup>, i.e. the diatomic oxygen radical anion, which react rapidly with airborne VOC and PM<sub>x</sub> species. The significance of air ionization chemistry and its potential for contributing to significant improvements in Indoor Air Quality will be discussed using case histories.

## INTRODUCTION

Air Ionization: Where We're Coming From ...

“Although the electrical discharge in gases has been investigated in its various phases ever since the study of electricity itself began, it is only in the last five or six years that our knowledge of the subject has begun to take systematic and satisfactory form. Careful observations has been made by hundreds of physicists, and the scientific literature abounded with descriptions of phenomena of great interest and undoubted scientific importance. But our knowledge of the subject consisted of a mass of *isolated* facts; no satisfactory underlying theory had been found by which these facts could be correlated.”

-- Earnest Merritt, on reviewing the new book by J.J. Thomson (Lord Kelvin), “The Discharge of Electricity Through Gases”, Charles Scribner’s Sons, New York, 1899; Science 9, 289-1 (1899).

Ionization phenomena involving reactive ions, radicals, and molecular species are encountered in diverse fields of meteorology, climatology, chemistry, physics, engineering, physiology, and industrial hygiene. Reports describing ionization in outdoor ambient and indoor air environments are scattered throughout the literature, both in diverse fields of endeavor, and across decades of time, making evaluations and comparisons difficult. The biology of small air ions and radicals has been reviewed (1, 2, 3, 4, 5, 6). Recent developments in air ion generation through engineered processes, coupled with increased interest in controlling VOCs and PM<sub>x</sub>, have kindled an awakening in advanced technology for improving the air quality of indoor environments (7, 8, 9). The current paper first provides background on the physics and chemistry of air ions. Applications of air ionization for air cleaning and treatment of VOCs and PM<sub>x</sub> are then presented in a series of case studies.

## PHYSICS OF AIR IONS

Most matter in the universe is “ionized”. In the high vacuum of space, atoms and molecules are present in excited energized states and possess electrical charges. By contrast, most matter on earth (and in the earth’s atmosphere) is un-ionized. A source of sufficiently high energy is required to induce ionization and separation of charge. Energy can be supplied by either natural or artificial (anthropogenic) sources, as derived from nuclear, thermal, electrical, or chemical processes. Specific energy sources include: cosmic radiation; ionizing (nuclear) radiation from earth sources, UV light, frictional charging by wind, water droplet breakup (waterfalls, showers), electrical discharge (lightning), combustion (fire, burning gas jets, engines), and strong electrical fields (corona).

Human additions and subtractions of ions in air environments include:

- Combustion processes: simultaneous generation of both ions and particles, the latter also tend to scavenge ions, e.g. smoking, candles.
- Indoor environments: synthetic décor and artificial ventilation can deplete space charge.
- Other situations: transmission lines produce ion plumes; video displays deplete local charges.
- Specific devices: produce air ions for air cleaning or charge neutralization.

Engineered devices for artificial air ionization are more controllable than natural processes. Recent developments in large ion generator design and operation have led to the commercial availability of energy-efficient units which can now produce controlled outputs of specific ions on demand, while minimizing the formation of undesirable byproducts, such as ozone. Ion generators have been used in a number of applications to control surface static charges. Air ionizers (ion generators) are being used more extensively to clean air in indoor environments.

Ionization is the process or result of a process whereby an electrically neutral atom or molecule acquires either a positive or negative electrical charge. Ionization occurs when energy in excess of the electron potential is absorbed by an atom yielding a free electron and a positive atom. The ions of the atmosphere have been of scientific interest for more than a century (10). The term “air ions” refers broadly to all airborne particles which possess electrical charge and whose movement is influenced by electric fields (11).

The chemical evolution of air ions, whether created naturally outdoors, or artificially indoors, depends on the composition of each environment, and especially on the types and concentrations of trace species. Specific reactions depend upon the physical properties of individual atoms and molecules, e.g. ionization potential, electron affinity, proton affinity, dipole moment, polarizability, and chemical reactivity. The primary positive ions,  $N_2^+$ ,  $O_2^+$ ,  $N^+$ , and  $O^+$ , are very rapidly converted (microseconds) to protonated hydrates,  $H^+ \cdot (H_2O)^n$  ( $n < 10$ ), while the free electrons quickly attach to oxygen to form the superoxide radical anion,  $^3O_2^-$ , which also can form hydrates (12). These intermediate species are collectively called “cluster ions”.

Cluster ions can react further with trace volatile and particulate constituents. A cluster ion may collide with as many as 1,000,000,000,000 ( $10^{12}$ ) molecules in air at ground level during its brief (~ one min) lifetime (11). Chemical-, nuclear-, photo-, and electro-ionization processes are used to separate and identify chemical spectra. Molecular disassociations and reactions in the gas phase and on particulate surfaces greatly complicate overall reaction schemes in real-world atmospheres. Ion chemistry continually changes through chemical reactions, molecular rearrangements, and growth of molecular ion “clusters” and ionically charged particulates. The protonated hydrates may be about 1 nm (0.001  $\mu\text{m}$ ) in diameter and have electrical mobilities of 1-2  $\text{cm}^2/\text{V}\cdot\text{s}$ . The ion clusters may be about 0.01 - 0.1  $\mu\text{m}$ , with mobilities of 0.3 -  $1 \times 10^{-6}$   $\text{m}^2/\text{Vs}$ . The later are larger in physical size, but orders of magnitude less electronically mobile. By comparison, common fog droplets or dust particles may range up to 10 $\mu\text{m}$  in size.

The combined presence of ions and electrons results in space charge, i.e. the total free unbalanced charge existing in the atmosphere. Both unipolar positive or negative space charge densities can be measured. Fair weather values for air ions at sea level are ~200-3,000 ions/ $\text{cm}^3$  of both polarities. Small ions increase significantly during rainfall & thunderstorms due to natural activation: negative ions may increase to 14,000 ions/ $\text{cm}^3$ , while positive ions may increase to 7,000 ions/ $\text{cm}^3$ . The ratio of positive to negative air ions at ground level normally is about 1.1-1.3, decreasing to about 0.9 following certain weather events. Smoking one cigarette can reduce air ions in a room to ~10-100 ions/ $\text{cm}^3$ .

Small ions and ion clusters have numerous opportunities for collision and reaction with any air impurity, i.e. essentially any and all constituents in the atmosphere. They are removed from the atmosphere through reaction with other volatile constituents, or through attachment to larger particles by diffusional charging and field charging. Lifetimes of ions are shorter, the higher their concentrations (or conversely, lifetimes are longer, the lower their concentrations, i.e. less chance of hitting something). The lifetimes of air ions are strongly dependent on humidity and temperature, and the relative concentrations of trace volatile and particulate species. Typical lifetime of a naturally generated small air ion in clean air is ~100-1000 s.

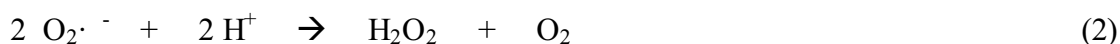
## CHEMISTRY OF AIR IONS.

“Oxygen” is required by most life forms. There is a dynamic balance, however, between generation of any oxygen species necessary for life on one hand and protection against its toxic effects on the other (13, 14). Four oxidation states of molecular dioxygen are known:  $[\text{O}_2]^n$ , where  $n = 0, +1, -1, \text{ and } -2$ , resp., for dioxygen, dioxygen cation, superoxide anion, and peroxide dianion (symbolically expressed as  ${}^3\text{O}_2$ ,  ${}^3\text{O}_2^+$ ,  ${}^3\text{O}_2^-$ , and  ${}^3\text{O}_2^{2-}$ ). In addition, “common” oxygen in air,  ${}^3\text{O}_2$ , is in a “ground” (not energetically excited) state. It is a free “diradical” having two unpaired electrons. The two outermost pair of electrons in oxygen have parallel spins indicating the “triplet” state (the preceding superscript “3”, usually omitted for simplicity). Oxygen itself is a common terminal electron acceptor in biochemical processes. It is not particularly reactive, and by itself does not cause much oxidative damage in biological systems. It is a precursor, however, to other oxygen species that can be toxic, including: superoxide anion radical, hydroxyl radical, peroxy radical, alkoxy radical, and hydrogen peroxide. Other highly reactive molecules include: singlet oxygen,  ${}^1\text{O}_2$ , and ozone,  $\text{O}_3$ .

Ordinary oxygen does not react well with most molecules, but it can be “activated” by the addition of energy (naturally or artificially derived; electrical, thermal, photochemical, or nuclear), and transformed into reactive oxygen species (ROS). Transformation of oxygen into a reactive state upon addition of a single electron is called reduction (Eqn. 1). The donor molecule that gave up the electron is oxidized. The result of this monovalent reduction of triplet oxygen is superoxide,  $O_2^{\cdot -}$ . It is both a radical ( $\cdot$ , dot sign) and an anion (charge of  $-1$ ).



The superoxide radical anion is quantitatively the most important radical formed in humans – a 70 kg adult synthesizes at least 10 kg(!) per year (15). Approximately 98% of the oxygen consumed by respiring mitochondria is converted to water; the remaining 2 % results in superoxide formation through side reactions in the respiratory chain (16). Human cells constantly produce superoxide (and the reactive molecules derived from it) as an “antibiotic” against invading microorganisms. The biology of small air ions and oxygen radicals has been reviewed (Krueger and Reed, 1976). Superoxide also acts as a signaling molecule, along with  $NO\cdot$ , to regulate many cellular processes. Under biological conditions, it reacts with itself to produce hydrogen peroxide and oxygen through a reaction (Eqn. 2) known as “dismutation”, which can be spontaneous, or catalyzed by superoxide dismutase (“SOD”).



Superoxide is both an oxidant (electron acceptor) and a reductant (electron donor). It is important in the production of the highly reactive hydroxyl radical ( $HO\cdot$ ), as catalyzed by metallic ions and/or by sunlight. Superoxide reacts with nitric oxide radical ( $NO\cdot$ ) in vivo producing peroxynitrate ( $OONO\cdot$ ), another highly reactive oxidizing molecule. Superoxide can undergo further reduction to peroxide ( $O_2^{-2}$ ), an activated form of oxygen, usually described as “hydrogen peroxide” ( $H_2O_2$ ), in aqueous systems, where it is also necessary for health.

Superoxide is the dissociated form of a weak acid, the hydroperoxyl radical,  $HO_2\cdot$ . In aqueous systems, the relative proportions of these two species depend upon pH, and the appropriate equilibrium constant. Superoxide also can be formed by negative air ionization (17). The generation of low concentrations of hydrogen peroxide in wet air subjected to negative air ionization also has been confirmed (18, 19).

In the absence of metallic impurities, a solution of superoxide in strong alkali can be kept in the refrigerator overnight. By contrast, superoxide ion clusters in air react rapidly with airborne particulates and volatile organic species. While hydrogen peroxide is an oxidizing agent, the combination of hydrogen peroxide and superoxide (Eqn. 3) yields a much more reactive species, the hydroxyl radical, one of the strongest known oxidants.



Identifications of the individual chemical species that might be involved in chemical reactions in air environments are not trivial. Modeling of the reaction scheme may involve dozens of homogeneous and heterogeneous reactions amongst species including those mentioned above.

## REACTIVE OXYGEN SPECIES.

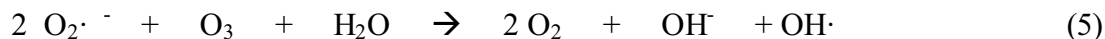
Oxygen, superoxide, peroxide, and hydroxyl species are all “Reactive Oxygen Species” (ROS), that can participate in a potpourri of oxidation-reduction reactions in both gaseous and aqueous phases (8, 20, 21). These active species are significant in the atmospheric destruction of organics, the removal of particulates, the formation of “smog”, and the destruction of ozone (O<sub>3</sub>). The hydroxyl radical is key to the tropospheric destruction of volatile organic compounds through a series of complex chemical reactions involving oxidation (abstracting electrons from organic compounds), which in turn can react with other organic molecules in a chain reaction.

The chemistries of reactive oxygen ions are found from “inner” to “outer” space. Solid-state sensors of the SnO<sub>2</sub> type, commonly used to “sense” trace gases, are affected by chemisorption of oxygen and water vapor. At sufficiently high operating temperature, O<sub>2</sub> from air is adsorbed onto crystalline surfaces having negative charges. Donor electrons in the crystals are then transferred to the adsorbed O<sub>2</sub> forming superoxide radicals that react with CO, hydrocarbons, and other trace gases or vapors. The resulting liberation of electrons decreases the surface charge and produces an increase in conductance that is then “sensed”. Similar chemistries are encountered in photocatalytic oxidation processes (22, 23), solid oxide fuel cells, and various nonthermal plasma processes.

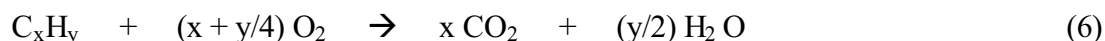
Space scientists have postulated that the unusual reactivity of the Martian soil and the absence of organic compounds are explained by ultraviolet radiation which causes oxidation of metal atoms and the creation of reactive oxygen species on the soil grains (24). The three radical species most commonly formed by UV in the presence of oxygen are: O<sup>·-</sup>, O<sub>2</sub><sup>·-</sup>, and O<sub>3</sub><sup>·-</sup>, sometimes collectively referred to as Reactive Oxygen Species (ROS). O<sub>2</sub><sup>·-</sup> is the least reactive, the most stable, and the most likely oxygen radical species to be encountered at ambient temperatures on earth. Its chemistry involves reaction with water to form hydrated cluster ions (25). Two associated species, hydroperoxide and hydroxide, are capable of oxidizing organic molecules. Superoxide reacts with water (Eqn. 4) to produce oxygen, and perhydroxyl and hydroxyl radicals, which are easily capable of oxidizing organic molecules.



Superoxide may also react directly with ozone to form hydroxyl radicals (Eqn. 5).



A composite scheme (Eqn. 6) involving several of the reactions described above might be postulated in which superoxide, generated by air ionization, causes the oxidation of volatile organics associated with airborne particulates having metallic inclusions:



This is a simplistic representation. For any given reactive oxygen species (ROS), there exists some confirmed or postulated reaction scheme for interconversion to any of the other species.

The speciation of individual VOCs, both before and after air ionization, i.e. the disappearance of parent species and the formation of byproduct species, other than carbon dioxide and water, has been speculated upon and modeled (26, 27, 28, 29). The impact of electron-driven chemistry was the subject of a recent workshop (30). It was stated to be “well-known” that non-thermal, gas-phase plasmas that are electronically generated at ambient temperatures and atmospheric pressure, can destroy low concentrations of VOCs. Destruction of ten VOCs (10-100 ppmv) at ambient temperature and atmospheric pressure in a packed-bed pulse corona reactor also has been reported (31). Destruction and removal efficiencies (DREs) were roughly estimated by chemical ionization potential. Ionization and other corona processes were particularly applicable to treating air containing relatively low initial concentrations (<100 ppmv – 10 ppbv). Chemical compounds that are reported by a number of private and governmental researchers to be amenable to treatment, i.e. to be chemically altered or destroyed by air ionization or allied processes, represent a diversity of chemical compounds (Table I).

**Table I. Chemical Compounds Amenable to Treatment by Air Ionization (\*).**

<b>No.</b>	<b>Chemical</b>	<b>MF</b>	<b>No.</b>	<b>Chemical</b>	<b>MF</b>
1	Carbon monoxide	CO	16	Naphthalene	C <sub>10</sub> H <sub>8</sub>
2	Nitrogen Oxides	NO, NO <sub>2</sub>	17	Ethylene	C <sub>2</sub> H <sub>4</sub>
3	Ammonia	NH <sub>3</sub>	18	Pinene (α-)	C <sub>8</sub> H <sub>14</sub>
4	Methane	CH <sub>4</sub>	19	Formaldehyde	CH <sub>2</sub> O
5	Ethane	C <sub>2</sub> H <sub>6</sub>	20	Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O
6	Butane	C <sub>4</sub> H <sub>10</sub>	21	Methyl Alcohol	CH <sub>3</sub> O
7	Pentane	C <sub>5</sub> H <sub>12</sub>	22	Methyl Ethyl Ketone	C <sub>3</sub> H <sub>8</sub> O
8	Hexane	C <sub>6</sub> H <sub>14</sub>	23	Methylene Chloride	CH <sub>2</sub> Cl <sub>2</sub>
9	Cyclohexane	C <sub>6</sub> H <sub>12</sub>	24	Trichloroethane (1,1,1-)	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>
10	Benzene	C <sub>6</sub> H <sub>6</sub>	25	Trichloroethane (1,1,2-)	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>
11	Toluene	C <sub>7</sub> H <sub>8</sub>	26	Carbon Tetrachloride	CCl <sub>4</sub>
12	Xylene (o-,m-,p-)	C <sub>8</sub> H <sub>10</sub>	27	Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>
13	Trimethylbenzene, 1,2,4-	C <sub>9</sub> H <sub>12</sub>	28	Hexafluoroethane	C <sub>2</sub> F <sub>6</sub>
14	Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	29	FC-12B	CClBrF <sub>2</sub>
15	Styrene	C <sub>8</sub> H <sub>8</sub>	30	CFC-113	C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>

(\*) Reported treatment efficiencies vary with initial concentration, relative humidity, and oxygen content.

Air ionization is expected to follow similar mechanisms, involving both bipolar ions, and free radicals, to oxidize organic compounds to intermediate byproducts and eventually to terminal products of carbon dioxide and water. Four processes involving reactions with air ions include: (i) recombination with other air ions, (ii) reaction with gaseous molecules, (iii) attachment to larger particles, and (iv) contact with a surface. The former two processes may be involved in the removal of volatile organic compounds; the latter two processes may be involved in the removal of particulate matter.

## OPERATION OF AIR IONIZERS.

Bipolar air ionizers create charged air molecules. By either adding or removing an electron, air molecules are given a negative or positive charge. Three different types of ionization systems currently used include: photon ionization, nuclear ionization, and electronic ionization. Photon ionization uses a soft x-ray energy source to displace electrons from the gas molecules. Nuclear ionizers use polonium-210 radiation sources to create alpha particles that collide with the gas molecules, displacing electrons. The molecules that lose electrons become positive ions. Neutral gas molecules rapidly capture the electrons and become negative ions. These types of ion generators do not have emitter points, so deposits are not a concern. However, x-ray and nuclear sources must be carefully installed and controlled to avoid creating safety hazards.

The electronic ionizer, or corona-discharge ionizer, uses a high-voltage applied to sharp emitter points or grids to produce a strong electric field. This field interacts with electrons of adjacent gas molecules, producing ions of the same polarity as the applied voltage. These ionizers are classified according to the type of electrical current that is applied to the emitter: pulsed DC, steady-state DC, or AC. AC devices are bipolar ionizers in that they alternately produce clouds of negative and positive ions with each cycle. The formation of other chemical species is affected by the type of current, the mode of action, the concentration of unipolar ions, the ratio of positive to negative ions, and the relative humidity. AC ionizers, the oldest type of electronic ionizer in common use, have inherent voltage swings as the electric fields produced move from positive to negative maximums unless otherwise controlled.

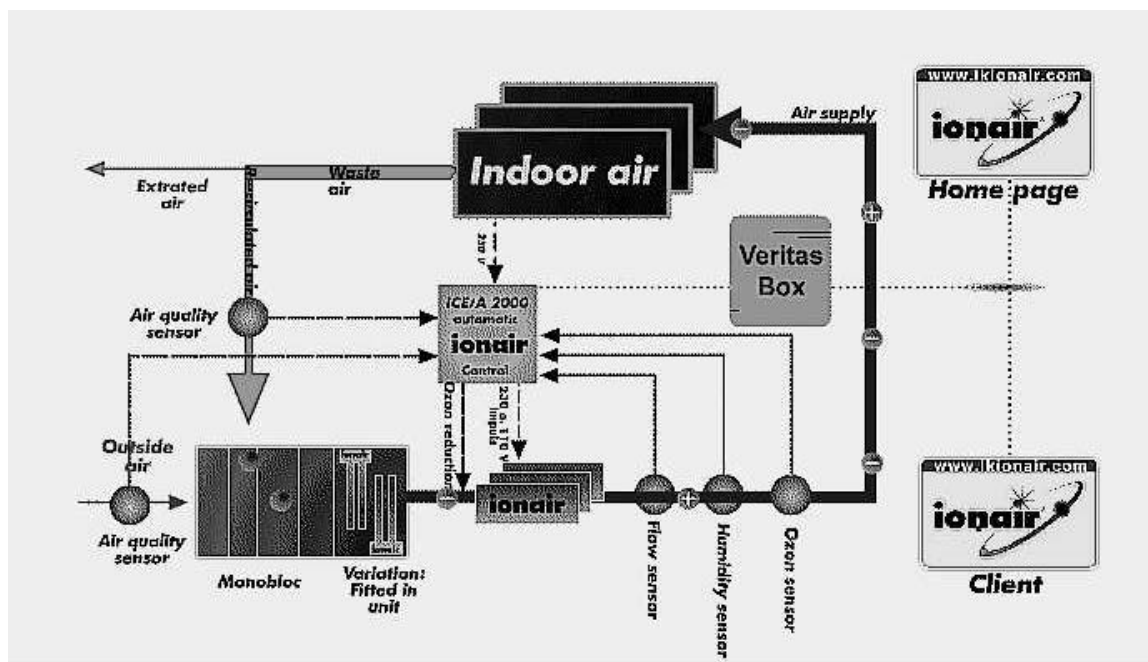
Air ion generation is measured with charged-plate monitors, as defined in the ESD Association Ionization Standard, ANSI EOS/ESD S3.1-1991. An alternative uses an electrostatic-field meter to measure static decay on glass substrates. One example (Ionmeter T-111, Transjonic AB, Källered, Sweden) is capable of monitoring ions to a resolution of  $\pm 20$  ions/cm<sup>3</sup>. Monitoring of ions allows for the generation of sufficient ions on demand for optimum performance.

It is important to distinguish among the various types of electronic air cleaners (32, 33, 34). Air ionizers, electrostatic precipitators, and ozone generators, are often lumped together, but have distinct differences in modes of operation (7). Valid issues have been raised on ozone toxicity (35, 36), the utility of ozone generators (37, 38, 39, 40), and reactions among indoor pollutants (41, 42, 43).

Air ionization processes have multiple components: sensors for monitoring air quality (VOCs and PMx), electronic monitoring of air ions, and ionization modules to generate ions on demand. The ionair® Air Ionization System (LK Luftqualität Air Quality, Inc., Luzern, Switzerland) (Figure 1) is an example of an automatically controlled ionization system to provide comfortable climates, reduce microbial contamination, and neutralize odors, by destroying and/or removing volatile and particulate constituents from indoor air environments. The air ionization treatment system is designed for flexible installation, either directly in an enclosed space or in the supply air from the central air handling unit (AHU). Air leaving the space can be either discharged directly to the atmosphere, or returned to the space after being mixed with outside air.

Locations of air ionization units can be tailored to a particular facility depending upon sources and strengths of VOCs and PM<sub>x</sub>. The air ionization appliances can be fitted directly into the central monobloc AHU to treat the entire airflow. Alternatively, the air ionization modules can be fitted into the existing ductwork downstream of the central HVAC system. Freestanding air ionization appliances can also be located in individual room spaces to meet immediate demands. Proper operation of an air ionization system to improve indoor air quality requires optimization of seven process variables describing both situation and demand. A process control unit is centrally located. Inputs can be set manually on the basis of situation design parameters and automatically on the basis of monitored demand parameters. Three manual inputs include: desired ion intensity level, power capacity, and airflow area. Four electronic inputs include: airflow, humidity, air quality, and ozone detection.

**Figure 1. Air Ionization – Process Schematic.**



A flow sensor measures volumetric airflow (cfm). A humidity sensor measures airborne water vapor. Air quality sensor(s) determine the relative demand for air ionization. Air quality sensors can be placed both in the return air duct and in the outside air intake. One type of air quality sensor (Figaro TGS 800, Figaro Engineering, Inc., Glenview, IL) can be used to measure levels of total volatile organic compounds (TVOCs) that can be oxidized by air ionization. Batterman and Peng, 1995). Another air quality sensor (optional) can be used to ensure that any ozone, that may be formed at low levels as an unintentional byproduct, is held well below OSHA limits. Yet another type of air quality sensor (optional) can be used to measure relative levels of certain size fractions of particulate matter (PM<sub>x</sub>) that can be removed by air ionization. Signals from the sensors can be logged by a personal computer. Responses of the ionization system can be visually displayed on a series of real-time plots and also stored for archival retrieval. Information would then be available to the client through the Internet using a standard web browser.



## CASE HISTORIES.

Air ionization technology has a long history in varied applications. The control of electrostatic discharges (charge neutralization by air ions) is important in sensitive manufacturing operations, such as semiconductors and nanomaterials. Air ionization is being applied for air cleaning where increasingly more stringent controls are being demanded. Volatile organic compounds (VOCs), such as odors, are oxidized by reactive oxygen species. Particulate Matter (PM<sub>x</sub>), such as environmental tobacco smoke (ETS), pollen, and dust, are agglomerated by air ions. Airborne bacteria and molds are inactivated. Other benefits include energy saving, by using less outside makeup air and generally increased comfort in indoor environments. Air ionization systems have been installed in domestic and office locations to improve indoor air quality, They have also been installed to control volatile and particulates in institutional, commercial and industrial locations. A short list of case histories illustrates the diversity of applications (**Table II**).

**Table II. Case Histories for Air Ionization.**

<u>Case History</u>	<u>Location</u>	<u>Application</u>
Engineering Center	Major city	Removal of specific VOCs
Billing Center	International airport	Removal of aircraft exhaust
Vintage Hotel	City center	Energy savings, improved IAQ
Modern Hotel	International airport	Removal of aircraft exhaust
Shopping Center	Metropolitan center	Control of VOCs; energy savings
Parliament Building	Capital city	Treatment of odors, VOCs, and microbes
Restaurant Complex	Central plaza	Removal of kitchen exhaust odors
Individual Restaurant	City center	Removal of kitchen odors, tobacco smoke
Meat Processing	Odor from waste	Inactivation of airborne microbes
Meat/Food Storage	Supermarket	Removal of odors, airborne microbes
Anatomy Laboratory	Medical school	Removal of formaldehyde
Pathology Laboratory	Hospital	Removal of airborne microbes
Soccer Stadium	Major city	Control of odors
Furniture Plant	Manufacturing site	Removal of tobacco smoke
Printing Plant	Small city	Removal of volatile cleaners
Hairdresser	Nail polishing	Removal of VOCs
Animal Handling	Research Laboratory	Removal of odors, airborne microbes

An air ionization system was installed in a large engineering center (Siemens AG, Berlin) with several hundred office workers in a multi-floor facility. Reductions in the levels of 59 specific VOCs representing nine broad classes of VOCs were quantitated (**Table III**). Specific VOCs were analyzed by GC/MS from samples collected on sorbent tubes during representative periods of operation with and without ionization. Although 31 of the 59 VOCs were initially below detectable limits, none were increased to above detectable limits. The TVOC level was reduced by 50 %. This is encouraging given the very low total initial level of 112 ug/m<sup>3</sup> and the target performance level of 300 ug/m<sup>3</sup>. The levels of 20 of the 59 specific VOCs were reduced and none were increased. No new VOCs were identified as products of incomplete ionization.

In addition, indoor levels of ozone were measured continuously in this facility during operational periods with and without air ionization. The arithmetic average over a one-month operation without air ionization was 0.7 ppbv, with a maximum of 5.8 ppbv. This can be compared to a regulatory standard of 100 ppbv. The arithmetic average over a one-month operation with air ionization was 6.6 ppbv, with a maximum of 14.4 ppbv. The levels in outside air were not measured directly but were calculated to be in the range of 10 – 20 ppbv.

**Table III. Case History A: Engineering Center (a).**

<u>Component (#)</u>	<u>Without Ionization, ug/m<sup>3</sup></u>	<u>With Ionization, ug/m<sup>3</sup></u>
Aromatics (13)	70	37
Alkanes (9)	5 - 1	4 - < 1
Iso-Alkanes (3)	4 - < 1	1 - < 1
Cyclo-Alkanes (3)	8 - 1	4 - 1
Alcohols (8)	< 10	< 10
Ketones (7)	< 10	< 10
Esters (3)	< 10	< 10
Chlorinated Hydrocarbons (9)	2 - < 1	2 - < 1
Terpenes (5)	3 - < 1	1 - < 1
Total VOCs (59)	112	56

(a) Analyses: Gesellschaft für Umwelt-und-Inneraumanalytik, Winkins & Kramer – GbR Monchengladbach.

Another case history involved a billing center near a major international airport (Visa, Zurich) where office workers were subjected to exhaust gases from ground transportation and airplane jet engines. Three representative VOCs were quantitated with and without ionization (**Table IV**). Significant reductions in noxious odors from partially burned fuel hydrocarbons were also noted.

**Table IV. Case History B: Travel Center (b).**

<u>Indoor Air Component</u>	<u>Without Ionization, ug/m<sup>3</sup></u>	<u>With Ionization, ug/m<sup>3</sup></u>
Isooctane	5.4	3.5
Benzene	8.3	3.5
Toluene	29.9	16.1

(b) Analyses: Okoscience Lufthygiene AG, Zurich.

Other investigations are currently in progress to obtain quantitative results for the removal of specific contaminants from a variety of applications. Anecdotal information is also accumulating from personal comments by practitioners and facility managers supporting significant reductions in odors and smoke, and perceived improvements in indoor air quality.

## SUMMARY.

Air Ionization: Where We're Going To ...

“The influence of physical forces, of modes of aggregation and of mass, not only on the result, but on the manner of the transformation of one kind of matter into another kind – in brief, *the conditions of chemical change* – present a problem to the chemist which only of late years has been submitted to experimental investigation. The difficulties besetting this line of inquiry are many, but the greatest of them is the difficulty of finding a reaction that is simple in kind, that takes place between bodies which can be prepared in great purity, and that yields products which can be exactly measured.”

-- H.B. Dixon, On Conditions of Chemical Change in Gases,  
Phil. Trans. Royal Soc. 175, 617 (1884).

Technologies for air cleaning have been cataloged (7, 32, 33, 44) by functionality and specificity for removal and/or destruction of  $PM_x$  and/or VOCs in indoor environments. Technologies include: (i) physical, (ii) physicochemical, and/or (iii) electronic processes, or combinations (**Table V**). Filtration of  $PM_x$  involves physical or mechanical collection of particles on porous or fibrous media. The mechanisms of removal are primarily impaction, settling, and diffusion. Gas-phase “filtration” involves sorption of VOCs onto surfaces of solid media, with or without chemical reactions. Chemisorbents are impregnated with chemically active ingredients, such as acids or bases, oxidants or reductants, or imbedded catalysts or photocatalytically active materials.

Electronic air cleaners can be cataloged further by types of ionization and modes of operation. Bipolar air ionization devices are the simplest, with others being variations of nonthermal plasma and corona discharge processes (45, 46). These devices produce local clusters of negative and/or positive ions. Cluster ions electrically charge  $PM_x$  thereby facilitating removal by filtration. Cluster ions also chemically react and destroy VOCs. This process, although similar to many familiar oxidation processes, is more subtle and complex. It can be effected at ambient temperatures without the need for solid catalysts. Air ionizers are distinct from electrostatic precipitators in that  $PM_x$  become electrically charged through direct contact with the air ions vis-à-vis attraction to electrically charged surfaces. Air ionizers also are distinct from ozone generators in that the active species are clusters of negative and/or positive air ions and not nascent ozone which is regulated for health reasons in indoor environments.

Air ionization technology, although well advanced, is just now entering the field of treatment of specific VOCs and  $PM_x$ , ranging from control of electrostatic discharges in sensitive manufacturing operations to destruction of hazardous air contaminants. Related technologies include oxidation in pulsed-corona reactors and other nonthermal plasma devices (47, 48, 49, 50). The benefits of air cleaning by air ionization are multiple: destruction, transformation, and removal of potentially hazardous VOCs and  $PM_x$ ; extended and improved performance of conventional technologies (filtration and adsorption); low energy costs; minimal bulk deposition of  $PM_x$  on room surfaces; less hazardous reactants and byproducts; and the potential for possible associated health benefits.

**Table V. Comparison of Air Cleaning Systems**

<b>System</b>	<b>Bipolar Air Ionization</b>	<b>Ozone Generation</b>	<b>Electrostatic Precipitation</b>	<b>Gas-Phase Filtration</b>	<b>Filtration</b>
<b>Function</b>	Electronic	Electronic	Electronic	Physicochemical	Physical
<b>Principle</b>	Barrier Discharge.	Sparking Discharge.	High-voltage wire and plate.	Selective sorption and reaction.	Flat, pleated, or HEPA media..
<b>Process</b>	(+) & (-) Ion generation.	Ozone generation.	Charging of particulate matter.	Sorption and reaction.	Collection on porous media.
<b>Active Species</b>	Bipolar ions and radicals ( $O_2\bullet^-$ )	Ozone ( $O_3$ ).	Charged particles	Sorption and reaction sites.	High surface area.
<b>Products</b>	$CO_2$ , $H_2O$ ; larger $PM_x$ .	$CO_2$ , $H_2O$ , $O_3$ .	Larger $PM_x$ .	Less VOCs.	Less $PM_x$ .
<b>Byproducts</b>	Minimal byproducts, $O_3$ if not controlled.	Significant $O_3$ , atm. reactants.	$O_3$ , if not cleaned regularly.	Spent media with contaminants.	Spent filters with contaminants.
<b>Health Concerns</b>	$O_3$ , limited by control.	High ozone exposure.	Exposure to high voltages and $O_3$ .	Saturation, capacity, disposal.	Contaminated filters, disposal.
<b>VOCs</b>	Chemical oxidation.	Chemical Oxidation	Sorption of VOCs on $PM_x$	Ad/absorption	NA
<b><math>PM_x</math></b>	Agglomeration.	NA	Collection on plates.	Collection in media.	Impaction, settling, and diffusion.
<b>Odors</b>	Oxidation	Oxidation.	NA	Ad/absorption	NA
<b>Microbes</b>	Inactivation.	Inactivation.	Particle removal.	NA	Particle removal.
<b>Control</b>	Ions on demand.	Continuous generation.	Process design.	Process design.	Process design.
<b>Costs</b>	Low	Low	Moderate	High	High
<b>Energy Needs</b>	Low	Moderate	High	NA	NA
<b>Energy Losses</b>	Low	Low	Low	High	High
<b>Maintenance</b>	Cleaning of tubes.	Replacement of elements.	Cleaning of plates.	Replacement of media.	Replacement of filters.

VOCs – Volatile Organic Compounds;  $PM_x$  – Particulate Matter (of size x,  $\mu m$ ).

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