Hard Ionization, Soft Ionization, and Byproduct Formation in Indoor Air Treatment

Abstract

Electrical air-cleaning technologies are often grouped together under the broad term "ionization," but this term can describe very different chemical processes. Older high-energy discharge technologies, including dielectric barrier discharge, corona discharge, and other non-thermal plasma systems, can create energetic electrons, radicals, ozone, excited species, and reactive oxygen and nitrogen compounds [1], [2], [3]. These species can fragment oxygen, nitrogen, water vapor, and volatile organic compounds, leading to secondary byproducts such as aldehydes, organic acids, oxidized VOCs, nitrogen oxides, ozone, and secondary organic aerosol [2], [5], [6]. In contrast, soft ionization technologies such as Targeted Bipolar Pulsed Ionization are designed to generate controlled positive and negative ions without operating as high-energy plasma decomposition reactors. The distinction follows the mature terminology used in mass spectrometry, where hard ionization intentionally fragments molecules and soft ionization is used to ionize molecules while minimizing fragmentation [7], [8], [9], [10]. This paper explains why hard ionization can produce undesirable byproducts and why soft, low-energy ionization is better suited for occupied-space air treatment when the goal is contaminant control without ozone or chemical byproduct formation.

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1. Introduction

The word "ionization" is often used too broadly in indoor air quality discussions. A dielectric barrier discharge reactor, a corona discharge ozone generator, a non-thermal plasma VOC abatement system, an electrostatic precipitator, and a tunable bipolar ionization system may all involve charged species, but they do not necessarily operate by the same chemistry.

The most important distinction is the amount of energy delivered into the gas phase. High-energy discharge systems can dissociate molecules and create reactive species. These systems are often intentionally used for VOC decomposition because they can generate oxidants and radicals that attack organic compounds. Reviews of dielectric barrier discharge and non-thermal plasma VOC abatement describe the formation of ozone and reactive oxygen species as central to the VOC degradation process [1], [2], [3].

This chemistry can be useful in industrial exhaust treatment, where the objective is to chemically destroy contaminants inside a controlled reactor. However, the same chemistry can be problematic in occupied indoor spaces. When VOCs are fragmented or partially oxidized, the outlet air may contain secondary byproducts rather than complete conversion to carbon dioxide and water [1], [2]. Indoor air studies have also shown that some ion-generating or oxidant-generating air cleaners can increase ozone, aldehydes, oxidized gases, or secondary organic aerosol under certain conditions [5], [6].

Soft ionization is fundamentally different. Rather than using high-energy plasma chemistry to fragment and oxidize compounds, soft ionization is intended to generate ions without breaking apart background gases or VOC molecules. Aeiro's Targeted Bipolar Pulsed Ionization, or TBPI, is positioned in this soft ionization category. Its purpose is to control ion polarity and timing so ions can be targeted toward contaminant classes without creating the high-energy chemical environment associated with ozone generation and VOC fragmentation.

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2. Hard Ionization

Hard ionization refers to an ionization process that deposits enough energy into a molecule to cause fragmentation. In mass spectrometry, the classic example is electron ionization, commonly performed at 70 electron volts. This technique intentionally produces molecular fragments, creating repeatable spectra used for compound identification. Mass spectrometry literature distinguishes hard ionization from soft ionization based on the degree of molecular fragmentation produced during ion formation [7], [8], [9], [10].

This distinction is directly relevant to air treatment. If an electrical discharge produces electrons, streamers, or microdischarges with enough energy to dissociate oxygen, nitrogen, water vapor, or VOCs, the process is no longer simply charging molecules or particles. It becomes a reactive chemical process [1], [2], [3].

In air, hard ionization can produce:

- atomic oxygen;
- ozone;
- hydroxyl radicals;
- superoxide;
- nitrogen oxides;
- excited oxygen and nitrogen species;
- fragmented VOC radicals;
- oxidized VOC intermediates;
- secondary organic aerosol precursors.

These species are useful when the goal is chemical destruction of pollutants, but they are not automatically desirable in occupied environments. A technology that is energetic enough to fragment VOCs can also create partial oxidation products that must be measured and controlled [2], [5], [6].

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3. Dielectric Barrier Discharge as a Hard Ionization Process

Dielectric barrier discharge is a common form of non-thermal plasma. It uses high voltage across a dielectric barrier to create many short-lived microdischarges. Although the bulk air temperature may remain near room temperature, the electrons generated in the discharge can have enough energy to initiate strong chemical reactions [1], [3].

DBD systems are widely studied for VOC abatement because they can generate reactive species capable of oxidizing organic compounds. Reviews of DBD VOC treatment describe the role of plasma-generated oxidants, including ozone and other reactive oxygen species, in VOC degradation [1], [2].

DBD is also a common ozone-generation method. DBD ozone generators work by dissociating oxygen molecules and allowing oxygen atoms to recombine with molecular oxygen to form ozone. A recent DBD ozone-generator study describes high-energy electron excitation and oxygen dissociation as part of the ozone-generation process [4].

This is the central problem with using hard ionization chemistry in occupied indoor air. If the process has enough energy to dissociate oxygen and form ozone, it may also have enough energy to fragment VOCs and initiate secondary chemistry [1], [2], [4].

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4. VOC Fragmentation and Secondary Byproducts

VOC removal by non-thermal plasma is rarely a simple one-step conversion of the VOC into carbon dioxide and water. Instead, it is a chain of reactions involving energetic electrons, radicals, ions, excited species, and oxidants. These reactions can break chemical bonds, abstract hydrogen atoms, add oxygen, and form unstable radical intermediates. Those intermediates can then react further to form secondary byproducts [1], [2], [3].

Potential byproducts from hard plasma VOC treatment can include:

- formaldehyde;
- acetaldehyde;
- formic acid;
- acetic acid;
- carbon monoxide;
- ozone;
- nitrogen oxides;
- oxidized VOCs;
- ultrafine particles;
- secondary organic aerosols.

The plasma-catalysis literature is useful here because it shows that researchers often add catalysts to non-thermal plasma systems specifically to improve selectivity, reduce ozone slip, and reduce undesirable byproducts. Reviews of plasma-catalytic VOC removal discuss both the mechanisms of VOC destruction and the importance of controlling byproduct formation [2], [3].

This is an important distinction for indoor air treatment. A hard plasma system may reduce the concentration of a target VOC, but target VOC reduction alone does not prove that the air is cleaner. A complete evaluation should also measure ozone, aldehydes, oxidized VOCs, acids, nitrogen oxides, particles, and other secondary products [5], [6].

Indoor air studies support this concern. Waring and Siegel found that a portable ion generator could increase ozone and, to a lesser degree, potentially aldehydes in a residential room under certain conditions [5]. Studies of oxidant-generating air cleaners have also reported formation of oxidized gases and secondary organic aerosol, reinforcing that air-cleaning technologies should be evaluated for both contaminant removal and unintended chemistry [6].

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5. The Mass Spectrometry Analogy

Mass spectrometry provides a mature and useful framework for explaining the difference between hard and soft ionization.

In hard ionization, such as conventional 70 eV electron ionization, the molecule receives enough excess energy to fragment. This produces a mass spectrum containing multiple fragment ions. Those fragments are useful because they help identify the original compound. Reviews of small-molecule mass spectrometry describe electron ionization as a hard ionization method and contrast it with softer methods used to preserve molecular-ion information [7], [8], [9], [10].

In soft ionization, the goal is different. The goal is to ionize, protonate, deprotonate, charge-transfer, or cluster the molecule while minimizing fragmentation. Soft ionization is preferred when the analyst wants to observe the intact molecular ion or molecular adduct rather than a cloud of fragments [7], [8], [10].

The same distinction can be applied to air-cleaning ionization:

Hard ionization uses enough energy to fragment gases and VOCs. It can generate ozone, radicals, oxidized VOCs, nitrogen oxides, and secondary byproducts [1], [2], [5], [6].

Soft ionization generates ions without intentionally fragmenting air molecules or VOCs. Its purpose is charge delivery and contaminant interaction, not chemical decomposition.

TBPI is a soft ionization technology because its design objective is low energy, controlled ion delivery, not plasma-driven chemical destruction.

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6. TBPI as a Soft Ionization Technology

Targeted Bipolar Pulsed Ionization is designed to deliver controlled ion output without operating as a high-energy plasma reactor. Unlike dielectric barrier discharge and aggressive corona discharge systems, TBPI is not intended to decompose VOCs by creating a highly reactive oxidation environment.

The key TBPI principles are:

Polarity control

TBPI can control whether positive or negative ions are generated, allowing the system to bias ion output toward the contaminant being targeted.

Pulsed bipolar operation

Instead of producing positive and negative ions simultaneously, TBPI can alternate polarity with a short delay between outputs. This reduces immediate ion recombination and allows more useful ions to move into the airstream.

Targeted contaminant interaction

TBPI is intended to use electrostatic attraction and ion-contaminant interactions rather than indiscriminate chemical oxidation.

Low-energy ion generation

TBPI should be described as a soft ionization process because it is designed to generate ions without entering the energy range associated with molecular fragmentation, oxygen dissociation, ozone formation, and VOC breakdown. This distinction is consistent with the hard-versus-soft ionization framework used in mass spectrometry [7], [8], [9], [10].

Occupied-space compatibility

Because TBPI is not designed to fragment gases or oxidize VOCs, it is better suited for occupied-space air treatment than hard ionization technologies that produce ozone or secondary chemistry [1], [2], [5], [6].

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7. Ozone as an Indicator of Hard Ionization Chemistry

Ozone is one of the clearest indicators that a discharge process is energetic enough to alter air chemistry. To form ozone from oxygen, the process must create reactive oxygen pathways, commonly through oxygen dissociation followed by recombination. DBD ozone generators are designed around this mechanism [4].

In an occupied indoor environment, ozone is undesirable for two reasons. First, ozone itself is a respiratory irritant. Second, ozone reacts with common indoor VOCs, including terpenes from cleaning products, fragrances, and building materials. These reactions can form formaldehyde, ultrafine particles, organic acids, and other oxidized compounds. Indoor chemistry studies have repeatedly identified ozone-initiated chemistry as an important source of secondary indoor pollutants [5], [6].

Therefore, avoiding ozone generation is not only a regulatory issue. It is also a way to reduce the likelihood of downstream secondary chemistry. A soft ionization system such as TBPI should be designed so that it does not create the energetic conditions required to dissociate oxygen. If oxygen is not being dissociated and ozone is not being formed, no VOC fragmentation and secondary oxidation byproducts is ensured [1], [2], [4].

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8. Why Soft Ionization Does Not Produce the Same Byproducts

Soft ionization does not rely on breaking molecular bonds. Its purpose is to create charged species at energy levels that do not fragment background gases or VOCs. This is the same basic distinction used in mass spectrometry, where soft ionization is selected to reduce fragmentation and preserve molecular-ion information [7], [8], [10].

In practical terms, TBPI is not intended to:

- split oxygen molecules;
- generate ozone;
- fragment VOCs;
- oxidize terpenes;
- create aldehydes;
- create organic acids;
- generate nitrogen oxides;
- form secondary organic aerosol.

Instead, TBPI is intended to:

- generate controlled ions;
- tune polarity based on contaminant type;
- reduce ion recombination;
- improve ion delivery;

- influence particles and contaminants through charge effects;
- support contaminant control without destructive gas-phase chemistry.

This is the core technical difference between hard and soft ionization. Hard ionization uses chemical decomposition and Soft ionization uses charge control.

TBPI is designed to avoid the energy regime associated with molecular fragmentation and ozone-forming plasma chemistry. Product-specific testing such as UL 2998 can confirm that ozone remains at or below background levels or method detection limits.

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9. Conclusion

Hard ionization and soft ionization are not the same. Hard ionization deposits enough energy into molecules to fragment them. In mass spectrometry, this is useful because fragmentation helps identify chemicals [7], [8], [9], [10]. In indoor air treatment, however, the same principle can create unwanted chemistry.

Older hard ionization technologies such as dielectric barrier discharge, PCO and aggressive corona discharge systems can fragment gases and VOCs. These processes may reduce certain contaminants, but they can also generate ozone, radicals, aldehydes, oxidized VOCs, nitrogen oxides, acids, and secondary particles [1], [2], [3], [5], [6].

TBPI is different. It should be understood as a soft ionization technology that controls ion polarity and timing without using high-energy plasma chemistry. Its purpose is not to chemically destroy VOCs through fragmentation, but to deliver targeted ions that interact with contaminants through charge effects.

The technical advantage of TBPI is that it avoids the energy regime associated with gas fragmentation, ozone generation, and secondary byproduct formation. This makes TBPI a more appropriate ionization approach for occupied indoor environments where the goal is improved air quality without adding reactive chemistry to the space.

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