

# CHLORINE DIOXIDE—Some History

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**1814:** Chlorine Dioxide is discovered by *Sir Humphry Davy*, when he adds sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to potassium chlorate (KClO<sub>3</sub>). It is an antimicrobial biocide recognized in the early 1900s. Since then it is well known for its disinfectant properties.



**1930's:** Beginning of more frequent use of *chlorine dioxide* for disinfecting areas. A major benefit of chlorine dioxide is that, as a true gas, it expands uniformly to fill the space it's disinfecting. Due to concerns about the logistics of safely transporting the gas, sodium chlorite began to be manufactured as a relatively safe precursor chemical, and the industries using chlorine dioxide would then generate the gas onsite as needed. Because of chlorine dioxide's solubility in water, it starts being used as a water treatment.

**1944:** First commercial application. Used as a Biocide/Taste and Odor Control agent *in domestic water at Niagara Falls in the USA*.

**1950's:** Begins extensive use of chlorine dioxide in *water treatment plants and swimming pools in the U.S.A.* Likewise it is discovered that chlorine dioxide *destroys biofilm*, the algal slime that collects in cooling towers, among other places and harbors harmful bacteria. Chlorine bleach by contrast cannot kill biofilm.

**1956:** Brussels, *Belgium*, switches to *chlorine dioxide* from chlorine for its *drinking water* disinfection operations. This marks the first large scale use of chlorine dioxide for potable water treatment.

**1967:** The Environmental Protection Agency (*EPA*) of the United States first registers chlorine dioxide as a disinfectant and sanitizer. The registration is for chlorine dioxide in the liquid form. Indicated uses include *food processing, handling and storage plants, bottling plants, washing fruit and vegetables, sanitizing water, controlling odors, and treating medical wastes*.

**1970's:** The *EPA* begins recommending using chlorine dioxide instead of chlorine bleach to *treat water*. Hundreds of municipal water systems successfully convert to chlorine dioxide. This *happens across the United States and Europe*; more so for the latter. The conversion is catalyzed by a safer environmental profile of chlorine dioxide over chlorine, because chlorine dioxide does not produce any harmful byproducts, as does chlorine bleach.

**1977:** Three thousand (3,000) municipal water systems achieving biological control using chlorine dioxide.

**1980's:** Chlorine dioxide gradually *replaces chlorine in many industries*—in the *pulp and paper industry* as a bleaching agent, in industrial water treatment as a biocide and as an odor control agent, in food processing as a sanitizer.

**1982:** National Library of Medicine (*NIH*). Chlorine dioxide was found "the relative safety of oral ingestion of chlorine dioxide and its metabolites, chlorite and chlorate, was demonstrated. PMID: 6961033 PMCID: PMC1569027 DOI: 10.1289/ehp.824657"

**1983:** The *EPA* recommends chlorine dioxide as a solution to *trihalomethanes* (THMs). When chlorine is used to *disinfect water and make it potable* (chlorination), THMs are produced as a by-product. THMs have been linked to cancer (i.e., they are carcinogenic). *Chlorine dioxide does not produce THMs.*

**1988:** The *EPA* registers chlorine dioxide as a *sterilizer*. This means chlorine dioxide is both *safe and effective to use in hospitals, healthcare facilities, and laboratories.*

**1988:** Adding Chlorine Dioxide to blood cells or to a solution of blood components, to a *blood collection bag*, to eliminate small *inocula* of bacteria, yeast or fungi from growing in a blood fraction, such as platelets during storage. (Patent US5019402A)  
Blood Banks centers where blood gathered as a result of blood donation, stored and preserved for later use in blood transfusion.

**1990:** Use of chlorine dioxide as a *disinfectant, sanitizer and sterilizer* grows across many industries and countries. Some of the industries are the *beverage industry, fruit and vegetable processing plants, pulp and paper industries*, and industrial waste treatment sites. These industries are spread across the *United States, the United Kingdom and Europe.*

**1993:** A method of parenterally *treating HIV* infections administering to a subject in need of such treatment an inhibition-effective amount of a chemically-stabilized chlorite matrix comprising an isotonic solution containing about 5 to about 100 mMol ClO<sub>2</sub> per liter of isotonic solution. (Patent US6086922A)

**1997:** National Library of Medicine (*NIH*). Chlorine dioxide was found to be highly effective against various organisms tested at very low concentrations in a minimum contact time of 30 seconds to 60 seconds. Escherichia coli was found to be more sensitive among the organisms tested. Concentration as low as 5 ppm also showed 100% killing of Staphylococcus aureus, which is known to be one of the resistant organisms.

**2001:** The Federal Emergency Management Agency (*FEMA*) and other government agencies use chlorine dioxide to *decontaminate buildings contaminated with Anthrax.* The chlorine dioxide was completely effective against the tiny Anthrax spores. The buildings, walls and furnishings suffered no damage from the treatment.

**2002:** National Library of Medicine (*NIH*) shows, "In a series of extensive human volunteer studies on water disinfectants, groups of 10 males received aqueous chlorine dioxide in drinking-water by a range of different protocols (a sequence of rising

concentrations of up to around 0.34 mg/kg body weight over a 16-day period, approximately 0.035 mg/kg body weight on every third day for 12 weeks, or approximately  $3.6 \times 10^{-5}$  mg aqueous chlorine dioxide/kg body weight per day daily for 12 weeks). Observations included physical examination (blood pressure, respiration rate, pulse, oral temperature, and electrocardiography), extensive blood biochemistry, hematology, and urinalysis, and the subjective recording of taste. There were no significant adverse effects recorded for any of the parameters measured."

**2005:** *FEMA* again uses chlorine dioxide. It is used to eradicate mold infestations in homes damaged by the flood waters from *Hurricane Katrina*. After a 12-hour treatment, a *New Orleans restaurant* is able to ***banish all mold*** inside without rebuilding.

**2004:** National Library of Medicine (*NIH*) shows that, thirty patients with chronic atrophic candidiasis/ were instructed to rinse the mouth with 0.8% ClO<sub>2</sub> mouth rinse (DioxiDent) twice daily for one minute and to soak their dentures overnight in the ClO<sub>2</sub> for 10 days. ClO<sub>2</sub> significantly improved the clinical appearance and microbial count ( $p < 0.001$ ) after treatment, without significant side effects, with total resolution in the majority of cases.

**2005:** National Library of Medicine (*NIH*) shows that, "The major chlorine dioxide by-products of concern are chlorite and chlorate. Chlorine dioxide reacts generally as an electron acceptor, and hydrogen atoms present in activated organic C-H or N-H structures are thereby not substituted by chlorine. Moreover, in contrast to chlorine, chlorine dioxide's efficiency for disinfection does not vary with pH or in the presence of ammonia, and it does not oxidize bromide. As opposed to chlorine, which reacts via oxidation and electrophilic substitution, chlorine dioxide reacts only by oxidation; this explains why it does not produce organochlorine compounds. In addition to this, chlorine dioxide is more selective in typical water treatment applications, as evidenced by its somewhat lower disinfectant demand as compared with chlorine."

**2010:** The United States Food and Drug Administration (*FDA*) issue a warning on using MMS according to Jim Humble protocols. They label it as industrial bleach. But at the same time ***they have approved the use of chlorine dioxide*** for use in ***mouthwashes, toothpastes, and as a food service disinfectant*** among other uses, citing it as being a better alternative than chlorine.

**2012:** The Red Cross collaborates in a study in Luuka District. Iganga, Uganda, Africa to determine a cure for Malaria using Chlorine Dioxide on 154 cases. Blood test shows 100% of patients have no Malaria after 4 days having been administer Chlorine Dioxide.

**2012:** Food and Drug Administration (*FDA*) says, Chlorine dioxide can be use "As an antimicrobial agent to be applied to ready-to-eat meats."

**2013:** National Library of Medicine (*NIH*) shows, "Chlorine dioxide is a size-selective antimicrobial agent. *Results:* The rate law of the reaction-diffusion model predicts that the killing time is proportional to the square of the characteristic size (e.g. diameter) of a

body, thus, small ones will be killed extremely fast. For example, the killing time for a bacterium is on the order of milliseconds in a 300 ppm ClO<sub>2</sub> solution. Thus, a few minutes of contact time (limited by the volatility of ClO<sub>2</sub>) is quite enough to kill all bacteria, but short enough to keep ClO<sub>2</sub> penetration into the living tissues of a greater organism safely below 0.1 mm, minimizing cytotoxic effects when applying it as an antiseptic. Additional properties of ClO<sub>2</sub>, advantageous for an antiseptic, are also discussed. Most importantly, that ***bacteria are not able to develop resistance against ClO<sub>2</sub>*** as it reacts with biological thiols which play a vital role in all living organisms. *Conclusion:* Selectivity of ClO<sub>2</sub> between humans and bacteria is based not on their different biochemistry, but on their different size. We hope initiating clinical applications of this promising local antiseptic. PMID: 24223899 PMCID: PMC3818415"

**2014:** National Library of Medicine (*NIH*) shows that, ClO<sub>2</sub> (40-110 ppm) significantly reduced postsurgical adhesion formation without affecting the strength of the healed wound.

**2014:** The Centers for Disease Control (*CDC*) registers ProKure V and PERFORMACIDE® as ***disinfectants against the Ebola virus***. Both contain chlorine dioxide. ProKure V claims it "begins to ***kill pathogens in a matter of seconds***, whereas other commonly used, more traditional disinfectants take minutes. The rapid speed in which ProKure V kills pathogens makes it a product of choice for ***helping contain infectious-disease*** outbreaks and keeping public facilities cleaner and safer for everyone." PERFORMACIDE® "is a unique chlorine dioxide generator and delivery system. Chlorine dioxide is a ***potent virucide***."

**2015:** National Library of Medicine (*NIH*) shows that, Non-confidential 2016 Chemical Data Reporting (CDR) information on the production and use of chemicals manufactured or imported into the United States. Chlorine dioxide: ***1 billion – 5 billion lbs.***

**2015:** National Library of Medicine (*NIH*) shows that, "Chlorine Dioxide is a Better Disinfectant than Sodium Hypochlorite against Multi-Drug Resistant Staphylococcus aureus, Pseudomonas aeruginosa, and Acinetobacter baumannii. ***In this study***, we evaluated and compared the antibacterial activity of chlorine dioxide (ClO<sub>2</sub>) and sodium hypochlorite (NaClO) on various multidrug-resistant strains in the presence of bovine serum albumin and sheep erythrocytes to mimic the blood contamination that frequently occurs in the clinical setting. The 3 most important species that cause nosocomial infections, i.e., methicillin-resistant Staphylococcus aureus (MRSA), multidrug-resistant Pseudomonas aeruginosa (MDRP), and multidrug-resistant Acinetobacter baumannii (MDRA), were evaluated, with three representative strains of each. At a 10-ppm concentration, ClO<sub>2</sub> drastically reduced the number of bacteria of all MDRP and MDRA strains, and 2 out of 3 MRSA strains. However, 10 ppm of NaClO did not significantly kill any of the 9 strains tested in 60 seconds (s). In addition, 100 ppm of ClO<sub>2</sub> completely killed all MRSA strains, whereas 100 ppm of NaClO failed to significantly lower the number of 2 MRSA strains and 1 MDRA strain. A time-course experiment demonstrated

that, within 15 s, 100 ppm of ClO<sub>2</sub>, but not 100 ppm of NaClO, completely killed all tested strains. Taken together, these data suggest that ***ClO<sub>2</sub> is more effective*** than NaClO ***against MRSA, MDRP, and MDRA***, and 100 ppm is an effective concentration ***against these multidrug-resistant strains***, which cause fatal nosocomial infections.

**2016:** Food and Drug Administration (***FDA***) says, Chlorine dioxide can be use "As an antimicrobial agent in water used in poultry processing." Also, "As an antimicrobial agent to be applied to red meat (including meat parts and organs), processed, comminuted, or formed meat products, and seafood."

**2017:** Food and Drug Administration (***FDA***) says, Chlorine dioxide can be use "As an antimicrobial agent in water used to wash fruits and vegetables that are raw agricultural commodities (RAC)."

**2017:** National Library of Medicine (***NIH***) shows," Efficacy and Safety Evaluation of a Chlorine Dioxide Solution. ***In this study***, a chlorine dioxide solution (UC-1) composed of chlorine dioxide was produced using an electrolytic method and subsequently purified using a membrane. UC-1 was determined to contain 2000 ppm of gaseous chlorine dioxide in water. The efficacy and safety of UC-1 were evaluated. The antimicrobial activity was more than 98.2% reduction when UC-1 concentrations were 5 and 20 ppm for bacteria and fungi, respectively. The half maximal inhibitory concentrations (IC<sub>50</sub>) of H1N1, influenza virus B/TW/71718/04, and EV71 were  $84.65 \pm 0.64$ ,  $95.91 \pm 11.61$ , and  $46.39 \pm 1.97$  ppm, respectively. A 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) test revealed that the cell viability of mouse lung fibroblast L929 cells was 93.7% at a 200 ppm UC-1 concentration that is over that anticipated in routine use. Moreover, 50 ppm UC-1 showed no significant symptoms in a rabbit ocular irritation test. In an inhalation toxicity test, treatment with 20 ppm UC-1 for 24 h showed no abnormality and no mortality in clinical symptoms and normal functioning of the lung and other organs. ***A ClO<sub>2</sub> concentration of up to 40 ppm in drinking water did not show any toxicity in a subchronic oral toxicity test.*** Herein, UC-1 showed favorable disinfection activity and a higher safety profile tendency than in previous reports."

**2020:** The country of ***Bolivia*** creates Law #1351—Rregulating the manufacture, marketing, supply and consented use of the Chlorine Dioxide (CDS) solution as prevention and treatment against the coronavirus pandemic (COVID-19). October 14, 2020 (<https://leyesdecretosbolivia.blogspot.com/2020/12/ley-n-1351-ley-que-regula-la.html>)

**2020:** Saving the world from ***Sars-COV-2*** and ***COVID-19*** with ***Andreas Kalcker's*** work with his last 14 year experience.