About Chlorine Dioxide

L-Care: the stabilised chlorine dioxide solution and its applications.

Abstract

This document describes the properties and applications of chlorine dioxide (ClO_2) with a special emphasis on its stabilized chlorine dioxide solution available under the trade name L-Care. This paper discusses the history of chlorine dioxide as a disinfectant, its properties and its fields of applications. It is also explained why chlorine dioxide is regarded as an ideal biocide and why its medical applications were delayed until now in spite of its advantageous properties as a biocide.

The history of chlorine dioxide ClO_2 and its fields of application

Chlorine dioxide is a greenish yellow gas, easily soluble in water and aqueous solutions. It had been known for long. In fact, the first recorded use of chlorine dioxide dates back to 1814 when Sir Humphry Davy first discovered the gas during an experiment, however it became well known in the twentieth century only. The largest quantities are used in the paper industry for whitening cellulose.[10]

Its second most important field of application is the disinfection of municipal water. For this purpose it was first used in the small town of Niagara Falls next to the Niagara Water Falls in 1944 substituting chlorine. Chlorine dioxide has many favourable properties compared to chlorine. Its disinfectant effect exceeds that of chlorine, moreover it does not chlorinate organic compounds.
In Niagara Falls the water used for potable water was contaminated with phenol, which caused the problem of a bad taste, because common chlorine disinfection transformed phenol into chlorophenol, which gave the water a really bad taste. What is more, during the chlorination of water so-called trihalo methane are formed, which are carcinogenic. It was therefore advisable to change over from the cheaper chlorine to the more expensive but healthier chlorine dioxide where the water contains a higher amount of organic materials.
This had been done first in 1956 in Brussels among the big cities. [10] [11] [12]

Application of ClO_2 in the food industry, oral hygiene and dentistry

Recently chlorine dioxide solutions were introduced for other purposes, like in the United States for washing fruits and meats. Besides disinfection chlorine dioxide can be used also for deodorizing, for mouthwash, and for other purposes. Chlorine dioxide not only kills all the bacteria responsible for bad breath but directly reacts with the sulphur containing compounds (like sulphur- hydrogen, methyl-mercaptan and dimethyl-sulphide) causing the bad breath, and this way successfully stops halitosis as demonstrated by a very thorough Japanese study [1]. The same paper emphasizes two important advantages of mouthwashes made with chlorine dioxide compared to those containing chlorohexidine: the former does not discolour the teeth and tongue and even its continuous use does not produce unwanted side effects. The wide spread of these mouthwashes has been hindered as besides chlorine dioxide they also contained other chemicals which unfavourably effect on one side the quality and on the other side the long term stability of these mouthwashes. To avoid problems caused by the instability chlorine dioxide can be prepared on the spot by mixing the necessary chemicals. This procedure is used e.g. by the DioxiCare [2] system of the Frontier Pharmaceutical firm in New York, which is recommended also for stopping toothache. The local production of chlorine dioxide solves only the problem of durability, however, the chemicals needed for the ClO_2 production still stay in the mixture, besides this aqueous solution is not stable and free unhealthy ClO_2-gas evaporates.

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Routine methods of ClO_2 production on the spot

ClO_2 can be produced on the spot in several ways. Here we only describe a method which is suitable for human purposes. The simplest way is adding some acid to sodium chlorite ($NaClO_2$) because $NaClO_2$ disproportionates into ClO_2 and Cl^- ion in acidic medium. Optimum yield and shortest reaction time would be achieved with hydrochloric acid but that can be used in industrial applications only. For human purposes hydrochloric acid is replaced with some organic acid, mostly citric acid. However, ClO_2 production with citric acid is slow and incomplete, which is problematic not only because of the low yield but mainly because of the unreacted chlorite staying in the solution. Moreover ClO_3^- is also formed which is also a toxic contaminating component. The biggest problem, however, is the citric acid itself which is rather harmful for tooth enamel. In addition, as we have already mentioned above, the chlorine dioxide solution produced this way is unstable because of its contaminants: it decomposes easily, evaporates as ClO_2-gas and this is why it must be produced on the spot and consumed as soon as possible. [10]

A new invention: L-Care

Our research, looking to the behaviour of water in nature and its anomalies, we were looking how to stabilise unstable solutions like high concentrates of salt (seawater), hardening lime solutes and also chlorine dioxide solutions. As a result we managed to develop a stabilisation technology/formulation capable to produce a stabilised ClO_2 solution. A patent is not applied for this method, seen back engineering is not possible and on expert advices. As advantage it does not decomposes or evaporates as ClO_2-gas as long it is stored outside direct sunlight and in a clean vessel and as result it has a long shelf life. The concentration of ClO_2 in L-Care can be more than 25.000 ppm.

Air can play a central role as a reservoir for potential harmful micro-organisms like the corona virus. The efficiency of the product ‘L-Care’ in cleaning the air from bacteria and fungi with the aid of a common electronic humidifier. 100% cleaning of the air from bacteria after 1h of humidification was reported with 10% (v/v) L-Care 2,5% in two testrooms: a lab room and an office room. In addition zero accumulation of ClO_2-gas was detected in the rooms during or after the humidification process. [4]

Before listing the possible applications, however, first we show why ClO_2 is one of the most effective disinfectants –maybe the most effective one–, that is “the ideal biocide”, and – despite its excellent properties – why it has not been used in human medicine.

Why ClO_2 is an ideal biocide?

First of all, ClO_2 can be successfully applied against all types of microbes – thus against bacteria, fungi, viruses and protozoa and usually it is more effective than other disinfectants.

Table I [5] shows for several disinfectants those minimal disinfectant concentrations in ppm (mass/mass) units which is necessary to achieve sufficient disinfectant effect within 2.5 minutes. The Table compares the effectiveness of various disinfectants for 5 different microorganisms.

The Table demonstrates that while in the case of chlorine dioxide often 1 ppm is sufficient, higher concentrations are needed using other disinfectants to obtain the same effect. Especially, during these days ethanol is broad used as hand disinfections, it is advised to use minimum 70% concentration. Replacing with a 1,5 ppm ClO_2 aqueous solution shows the same effect, but using less chemicals (eco-friendly) and without the adverse health effects of the other chemicals, like for alcohol-based hand sanitizers: irritation, vomiting, conjunctivitis, oral irritation, cough, and abdominal pain. Abuse of alcohol-based hand sanitizers by children can be equivalent to consuming roughly 60% liquor. [13]

Which means that among all the typical disinfectants displayed in the Table chlorine dioxide is the most effective one and without adverse effects.

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Table 1. Effect of disinfectants on Microorganism

Disinfectant [ppm]	Microorganism				
	E. coli	S. aureus	MRSA	B. subtilis (spore)	A. niger
Glutar-dialdehyde	100.000	100.000	100.000	100.000	100.000
Phenol	10.000	>10.000	>10.000	>10.000	>10.000
Abs. ethanol	500.000	500.000	500.000	500.000	500.000
Chlorine hexidine digluconate	100	10	1.000	1.000	>10.000
Benzalconium chloride	100	10	100	1.000	10.000
Polivynil pirrolidon (Povidon)	10	100	100	>1.000	1.000
Sodium hypochlorite	10	10	10	>1.000	1.000
Chlorine dioxide	1	1	1	100	10

The second very advantageous property of ClO_2 is that for humans it is not dangerous at all, at least not in a small quantity. As previously mentioned, chlorine dioxide is used mainly for disinfecting water, therefore first it was demonstrated with animal experiments – applying mostly rats– that it is practically harmless for mammals. For example, in one experiment [6] rats were drinking water containing chlorine dioxide over a period of 90 days and it did not make any harm in the animals even if the ClO_2 concentration was 200 ppm in their drinking water. The only symptom observed was the inflammation of the respiratory tract but that was not due to the water consumed but to the ClO_2 evaporated from water and inhaled subsequently. Nevertheless, when in the United States more and more cities switched to ClO_2 to disinfect municipal water then human experiments were also started in the beginning of the 1980's at the Ohio State University with 60 volunteer young men at the ages of 21 to 35 years [7]. They drunk 1 litre of water containing ClO_2, and after that they were subjected to very extensive clinical tests over 4 days. When no clinical change was found at anybody, they were asked to drink again 1 litre of water but with a higher concentration of ClO_2. This way increasing gradually the quantity of the ClO_2 it was concluded that consumption of 24 mg of ClO_2 (equal of drinking one litre with 24 ppm ClO_2) per day does not cause any measurable change in a healthy human being. The only reason why higher doses were not tested is that larger quantities cannot be consumed with drinking water, and the aim of these experiments was to prove that it is safe to use ClO_2 for the disinfection of municipal water.

Furthermore, it is important to mention that the report of the Agency for Toxic Substances & Disease Registry [8] states that ClO_2 is not carcinogenic and it is not an allergen either.

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The third advantageous property of ClO_2 is that while it dissolves very well in water which is one of the most polar solvents, at the same time it also dissolves very well in apolar organic solvents like hexane, cyclohexane, benzene [9] or silicon rubber [3]. Consequently it also dissolves well in the apolar lipid phase of the cell membrane which means that cell membranes cannot prevent the penetration of ClO_2 to the tissues. This is the reason why ClO_2 disinfects not only on the surface of the skin or mucous membranes, but it can disinfect in depth. It can penetrate – depending on the concentration and the time applied – to several tenths of a mm or even deeper into the skin. This is a most important property in the case of biofilms. For example, although ozone is accepted as the strongest disinfectant ever in free aqueous solutions, in case of biofilms it is almost ineffective, because the solubility of ozone is too small therefore it cannot penetrate into the biofilms. Chlorine dioxide on the other hand, is very effective against biofilms.

The fourth advantageous property of ClO_2 is that it reacts with very few materials. It oxidizes Fe(II) to Fe(III) and Mn(II) to Mn(IV) but it does not react (or reacts only very slowly) with alcohols, aldehydes, monounsaturated hydrocarbons and some more. Among the 20 amino acids, which occur in living beings, it only reacts with 4 but with those very swiftly. These 4 are the 2 amino acids which contain sulphur: the cysteine and the methionine (the attraction of ClO_2 to sulphur has been mentioned earlier), and also the aromatic tyrosine and tryptophan. Its disinfecting effect on bacteria, viruses, … can be attributed to these reactions, although the exact mechanism of the effect is not yet known.

If a disinfecting is carried out in a medium which contains materials that can be oxidised and chlorinated then ozone and chlorine will be consumed rapidly in the oxidising and chlorinating reactions so a lot of them is needed. ClO_2 on the other hand reacts with few materials only, so its consumption is low even under such conditions.

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The fifth very advantageous property of chlorine dioxide which should be emphasized is that microbes are not able to develop resistance against chlorine dioxide. This was established in the toxicological report [8] on the basis of experiments but this can be expected theoretically as well. Namely, all living creatures, including microbes are composed of the same 20 amino acids, so that none of them can live without cysteine, methionine, tyrosine and tryptophan. As chlorine dioxide reacts with these materials bacteria are not able to develop resistance against it. This can have special significance in our days, when new strains appear continuously, which are resistant to various antibiotics, like the well-known MRSA (also called the superbug in hospitals) and recently the corona virus SARS-CoV-2 and all its variants which all need the same amino acids to live and multiply.

Why ClO_2 was not broad applied until now?

After all that a logical question emerges, why has not chlorine dioxide been introduced as a disinfectant for humans, animals, household or in clean rooms long ago? We can list 4 reasons:

There was no method, whereby a pure enough aqueous chlorine dioxide solution could be easily and swiftly produced as a aqueous solution. Most products on the market are 2-component chemicals (a salt and an acid). This is not ideal for daily use or households, neither for daily industrial use. The introduction of L-Care solution solves these problems. L-Care is a ready to use product. Available in concentrations up to more than 25.000 ppm ClO_2.

It was believed that the aqueous solution of chlorine dioxide decomposes fast and therefore the aqueous solution cannot be stored. The L-Care, an aqueous stabilised ClO_2 solution can be stored at room temperature even for years without decomposition.

Big pharmaceutical companies are not interested in dealing with known molecules and ClO_2 has been known for two centuries, as these molecules cannot be patented and therefore the prospective profit is smaller.

Finally, a practical disadvantage of chlorine dioxide is its volatility. Namely, a chlorine dioxide solution is not stable, ClO_2 evaporates and this gas can be harmful and is explosive in high concentrates. Common ClO_2 solution is a dangerous good and transport is restricted. When the L-Care chlorine dioxide solution is applied, nothing evaporates, thus it can be regarded as an ideal safe biocide in this respect as well. Also aerosols made from L-Care do not produce free ClO2-gas.

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L-Care ClO_2 application?

L-Care has broad spectrum bactericidal and fungicidal power, as well as spores and veridical action and to be used in the disinfection of operating rooms, dressing rooms, cradle rooms, patient rooms, kitchens, dining rooms, warehouse, cooling rooms, refrigerators, disease control in agriculture and other cultivations, disinfection of fruit and vegetables, disease control during storage, water purifier, open/close cooling tower maintenance or any area requiring disinfection. Application is possible in any way, including spraying, aerosols, immersion, washing, ... The residual effect is up to more than 7 days.

After harvesting the fruits and vegetables, the contamination is more or less fast due to the activity of bacteria, fungi and spores in the environment, on top of the ones present in the packing material used for transport. The quality of the product will depend of what happens until it will be acquired by the consumer. A logical process of deterioration exist in the vegetal products in the market where the decomposition will depend of the quality and type of bacteria they contain, in order to nourish themselves, they will initiate an enzymatic process which allows them to convert the more complex foods into a simpler form. This process is known as Rotting or Decomposition. We know that most of the fruits and vegetables are eaten raw or with skin, which undoubtedly increases the risk for illnesses, as pathogenic micro-organisms are potentially dangerous and cause effects that has its consequences on the financial and wellbeing of the consumer. To present and to serve the public, healthy products is an important commitment the commerce and the food industry must make. To clean the facilities and the equipment means using products (detergents, soaps, etc.) that allow the hygiene but not the disinfection, wherefore the problem persists. The use of a good germicide is necessary (bactericide and fungicide) that possesses the properties of an optimum disinfectant. L-Care germicide of large spectrum is a nontoxic chemical product. Fruits and vegetables can be immersed in the prepared dilution. Disinfection through immersion is effective.

In the storage areas, cleaning the facilities and during the final rinse with L-Care diluted; you can power spray twice a week, through which you maintain a clean and disinfected warehouse. Cold chambers, can be disinfected via power spray with L-Care diluted, avoiding this way the spreading of fungi and inhibiting the smell of mold or humidity. In the boxes or bags (in polyethylene) used for the packing, a light and fast power spray is sufficient to render a problem free product to the consumer.

Transport requires special attention, for which a power spray of L-Care at the recommended
dilution resolves any possible sanitary problem.

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