# Sanitation of Juice Facilities for Presumptive Alicyclobacillus (TAB)
# Use of Chlorine Dioxide


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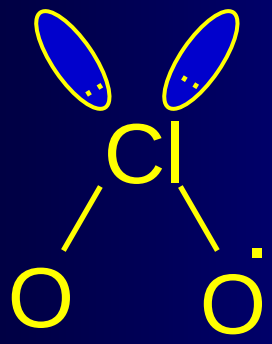
# Comparison of $ClO_2$ with Chlorine

## $ClO_2$

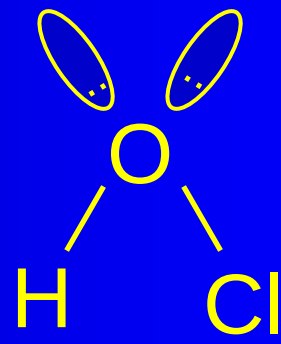



Chlorine dioxide

## $Cl_2$ ⟷ HOCl

Cl—Cl

Chlorine




Hypochlorous acid

↕

NaOCl

(Sodium hypochlorite)

# Reactions of $ClO_2$ Vs. Chlorine

1. $ClO_2$ reacts primarily by oxidation reactions which produce few, if any, volatile or nonvolatile chlorinated organics.

2. Chlorine reacts by oxidation and electrophilic substitution which may produce both volatile and non-volatile chlorinated organics. (e.g., THMs, dioxins, chlorinated phenols, trichloroacetic acid, chlorinated terpenes)

# Comparison of $ClO_2$ with Chlorine

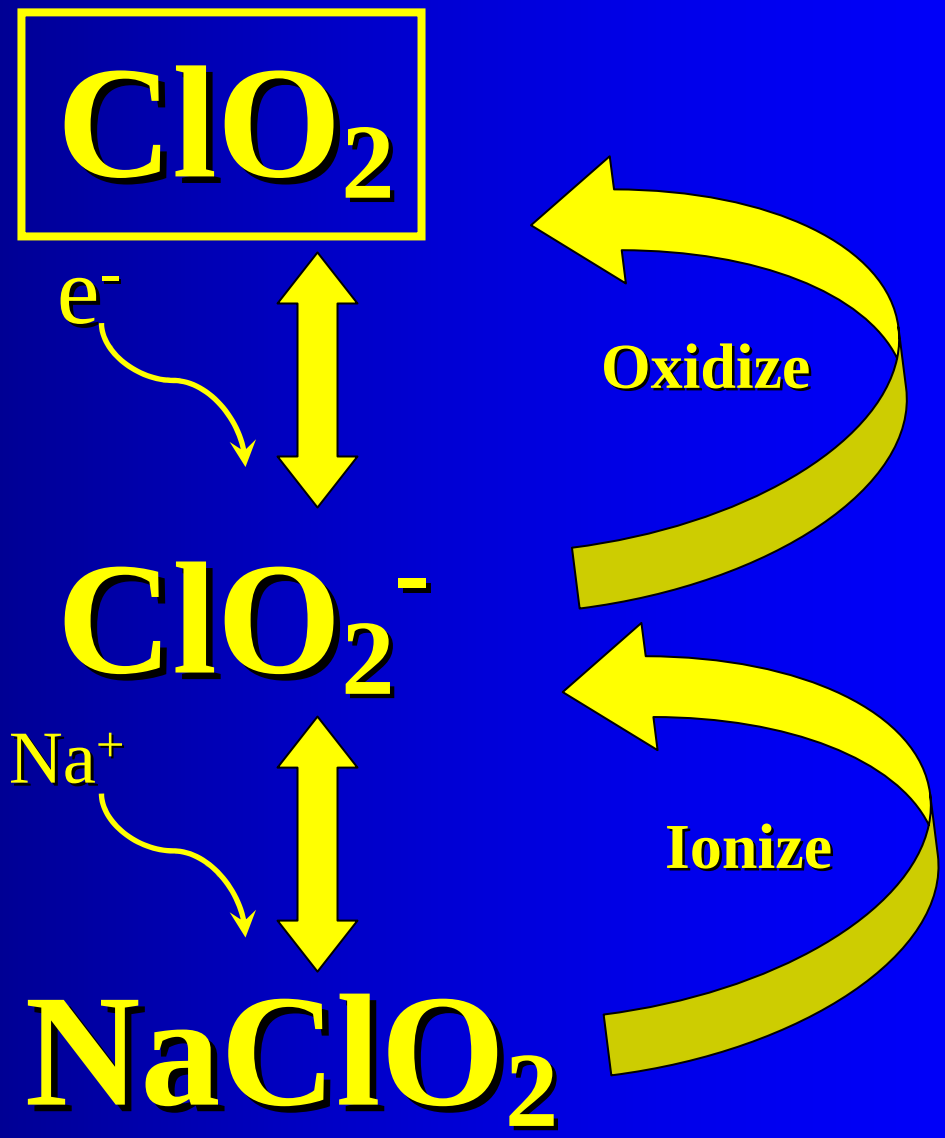
| Property | Chlorine Dioxide | Chlorine (HOCl) |
|---|---|---|
| • Primary Chemical Reaction | Oxidation Only, No Chlori-nated By-products. | Elecrophilic substitution resulting in Cl-byproducts |
| • Corrosion potential | Low ($E_0$ = 0.95V) | High ($E_0$ = 1.49V) |
| • Taste & Odor | Slight | Produces “chemical” taste |
| • Effective pH Range | 1-10 | 6.8-7.6 |
| • Reaction in Water | Does not hydrolyze | Hydrolyzes in water |
| • Reaction to Organic Load | Resists neutralization | Readily neutralized |
| • Reaction to Biofilms | Highly reactive | Largely ineffective |
| • Oxidative capacity | 2.63 | 1 |

# RedOx profile

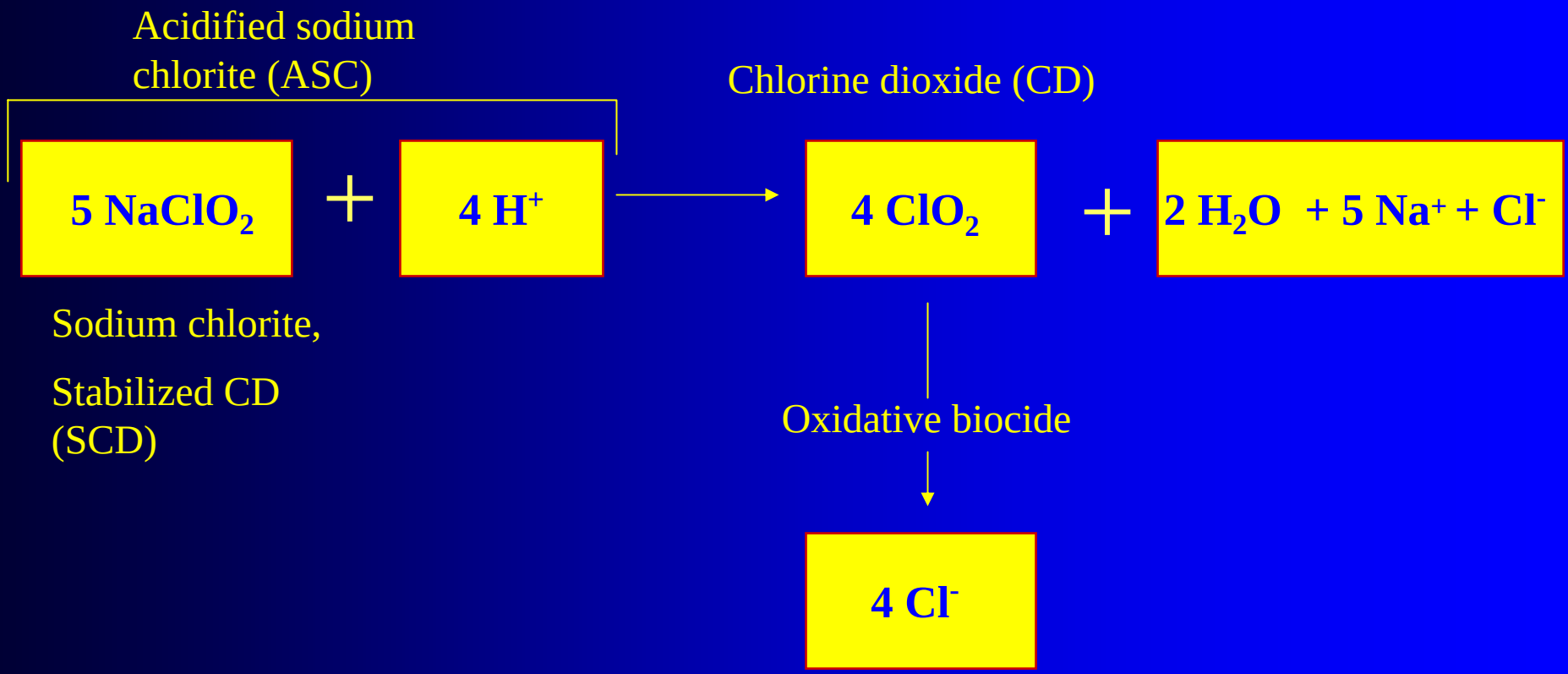
Chlorine Dioxide

Chlorite ion

Sodium chlorite



# Generation of Chlorine Dioxide




- Ultimate breakdown product is sodium chloride

# *A. acidoterrestris* Spore Population ($log_{10}$/mL) upon *In Vitro* treatment of $ClO_2$

( Lee *et al.*, 2004. Int. J. of Food Microbiol., 92, 121-127 )

| $ClO_2$ (ppm) | Treatment time (min) | | | |
|---|---|---|---|---|
| | 0 | 0.5 | 1 | 5 |
| 20 | 6.06 | 5.97 | 5.94 | 4.37 |
| 40 | 6.12 | 5.95 | 5.38 | 1.62 |
| 80 | 6.02 | 5.08 | 3.25 | <0.70 |
| 120 | 6.03 | 3.92 | 1.26 | <0.70 |

# Efficacy of $ClO_2$ on Apple Surface Innoculated with *A. acidoterrestris* Spores

(Population reported in $\log_{10}$/mL)

| | $ClO_2$ (ppm) | Treatment time (min) | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 5 |
| Red delicious | 0 | 6.76 | | | |
| | 40 | 5.00 | 3.64 | 2.40 | <2.0 |
| | 120 | <2.0 | <2.0 | <2.0 | <2.0 |
| Golden delicious | 0 | 6.76 | | | |
| | 40 | 5.00 | 3.64 | 2.40 | <2.0 |
| | 120 | <2.0 | <2.0 | <2.0 | <2.0 |

( Lee *et al.*, 2004. Int. J. of Food Microbiol., 92, 121-127 )

# Efficacy of $ClO_2$ on Apple Surface Innoculated with *A. acidoterrestris* Spores

(Population reported in $\log_{10}$/mL)

| | $ClO_2$ (ppm) | Treatment time (min) | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 5 |
| Gala | 0 | 6.78 | | | |
| | 40 | 5.58 | 3.74 | 2.40 | <2.0 |
| | 120 | <2.0 | <2.0 | <2.0 | <2.0 |
| Fuji | 0 | 6.81 | | | |
| | 40 | 4.82 | 3.37 | <2.0 | <2.0 |
| | 120 | <2.0 | <2.0 | <2.0 | <2.0 |

( Lee *et al.*, 2004. Int. J. of Food Microbiol., 92, 121-127 )

# In Vitro Efficacy of $ClO_2$ on *A. acidoterrestris* Spores

Concentration of available $ClO_2$ = 100 ppm

| | CFU/ml | log CFU/ml | log Reduction |
|---|---|---|---|
| Control | $1.2 \times 10^4$ | 4.10 | - |
| 30s contact | $3.4 \times 10^3$ | 3.53 | 0.57 |
| 2min contact | undetected | undetected | ~4.10 |

# Efficacy of $ClO_2$ on Orange Surface Innoculated with *A. acidoterrestris* Spores

Concentration of available $ClO_2$ = 100 ppm

| | CFU/sample | log CFU/sample | Reduction |
|---|---|---|---|
| Control | $3.0 \times 10^5$ | 5.5 | - |
| DI Water | $3.5 \times 10^5$ | 5.5 | 0% |
| $ClO_2$ | $3.9 \times 10^4$ | 4.59 | 80% |

# In Vitro Effect of $ClO_2$ Against *A. acidoterrestris*

Concentration of available $ClO_2$ = 30 ppm

| | |
|---|---|
| Untreated Control | $9.2 \times 10^5$ cells per ml |
| 1 minute exposure | $1.6 \times 10^4$ cells per ml |
| 10 minute exposure | $1.7 \times 10^1$ cells per ml |

Tanner *et al.,* 2001, University of Oklahoma.

# Comparison with Other Sanitizers

***Concentration (ppm) of biocide required for > 5 log reduction in 60 seconds***

| **Sanitizer** | ***P. aeruginosa*** | ***S. aureus*** | ***S. cerevisiae*** | ***E. Coli* (O157: H7)** |
|---|---|---|---|---|
| Available Chlorine Dioxide | 6 | 30 | 30 | 3 |
| Sodium Hypochlorite | 200 | 200 | 400 | 600 |
| Peracetic Acid | 30 | 60 | 300 | 20 |
| Dodecylbenzenesulfonic Acid & Phosphoric Acid | 40 | 80 | 600 | 90 |
| Octanoic Acid, Decanoic Acid, Citric Acid & Phosphoric Acid | 80 | 150 | 200 | 60 |

Source: Tanner, *et al.*; Dept. Of Microbiology, University of Oklahoma, Norman, OK & *J. Indst. Micro.* **1989**, *4*, 145-154.

# Comparison with Other Sanitizers

***Concentration (ppm) of biocide required for > log 5 reduction in 60 seconds***

| **Sanitizer** | ***P. aeruginosa*** | ***S. aureus*** | ***S. cerevisiae*** |
|---|---|---|---|
| Available Chlorine Dioxide | 6 | 30 | 30 |
| Acidified Quat | 150 | 1,200 | 300 |
| Phenolic Compound | 1,500 | 380 | 190 |
| Iodophor | 440 | 440 | 450 |
| Glutaraldehyde | 1,600 | 2,200 | 18,000 |

Source: Tanner, *et al.*; Dept. Of Microbiology, University of Oklahoma, Norman, OK & *J. Indst. Micro.* **1989**, *4*, 145-154.

# Regulatory Status on Direct Food-Contact

| | | |
|---|---|---|
| • Produce | 500 to 1200 ppm (ASC) | 21 CFR 173.325 |
| | 3 ppm (CD) | 21 CFR 173.300 |
| • Red Meat | 500 to 1200 ppm (ASC) | 21 CFR 173.325 |
| • Seafood | 40 to 50 ppm (ASC) | 21 CFR 173.325 |
| • Poultry | 50 to 1200 ppm (ASC) | 21 CFR 173.325 |
| | 3 ppm (CD) | 21 CFR 173.300 |
| • Potatoes | 200 to 400 ppm (ACD) | Section 18, FIFRA |

(ASC) Acidified Sodium Chlorite

(ACD) Available Chlorine Dioxide

# Regulatory Status for Indirect Food-Contact

| | | |
|---|---|---|
| • Food contact surfaces | 50 to 100 ppm (no rinse) | 21 CFR 178.1010 |
| • Process water chill water, glycol system, retort cooling water, etc. | 5 ppm | EPA label |

# Regulatory Status on Non-Food Contact Applications

| | | |
|---|---|---|
| • Lube additive | 20-40 ppm | EPA |
| • Environmental | 500 ppm | EPA |
| • Drains | 500 ppm | EPA |
| • Foot baths | 500 ppm | EPA |
| • Stored potable water | 5 ppm | EPA |
| • Odor control | varies | no approval required |

# Quantification of $ClO_2$

Manual sampling

1) Iodometric Titration (AWWA Method 4500)

2) Indicator based dip Sticks (tetramethylbenzidine)

3) Ion Chromatography

Online

1) Ion selective membrane

2) Amperometric/polarographic

3) Spectrophotometric ($\lambda_{max}$ = 360nm)

# Conclusions

- Chlorine dioxide is radically different from chlorine compounds in reactivity and mechanism of action.

- Chlorine dioxide is highly effective in killing *Alicyclobacillus* spores in aqueous suspensions and on fruit (apples and oranges), rapidly producing up to 5 $\log_{10}$ reductions while yielding no toxic by-product.

- Chlorine dioxide does not react with citrus oils to produce chloroterpene.

- Application (activation & delivery) procedure is critical for achieving success. The use of surfactant such as an acid anionic may enhance the efficacy.