Busting the myths of chlorine disinfection by Karen Rossington

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The ideal cleanroom disinfectant should have good broad spectrum efficacy against highly resistant bacterial spores. Additional requirements include a sterile option for grade A and B environments¹, non-flammable so it can be used over large areas with no health and safety concerns, also fast drying with short contact times to reduce the time taken for biodecontamination. However, in an ideal world, this cannot be traded for any problems with either equipment or operators and the wider environment in terms of disposal. Another requirement that shortens the decontamination process is if the disinfectant has no residue that needs to be removed or as a minimum is free rinsing.

The product will need to have in excess of a 12-month unopened shelf life and in excess of a three-month in-use shelf life to be practical to store and use. This ideal disinfectant would then need to be manufactured to the requirements of cGMP, be notified to the BPR² and provided in cleanroom compatible packaging in a variety of formats so it was suitable for use in all areas of the cleanroom. It goes without saying that this all needs to be achieved in a cost-effective formulation. Many people believe that this ideal sporicide does not exist and that a compromise must be made.

On first reflection, a chlorine-based disinfectant would not necessarily spring to mind as the disinfectant that meets all of these ideal needs. Sodium hypochlorite is the most widely used chlorine-based surface disinfectant but has some known

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drawbacks, notably it is inactive in organic matter, corrosive to some metals and will leave a particulate residue. However, all chlorine disinfectants are not the same. Advances in production methodologies have allowed the creation of a disinfectant that meets all of the aforementioned requirements.

History of chlorine disinfection

One of the first known uses of chlorine for disinfection was in the form of hypochlorite known as chloride of lime. John Snow used it in 1854^3 , after an outbreak of cholera to attempt to disinfect the Broad Street pump water supply in London. Claude-Louis Berthollet, in 1785, prepared a bleaching agent by dissolving Scheele's gas in water and in 1789 improved it by mixing it with a solution of caustic potash (KOH); this was carried out in a French chemical plant in Javel and was known and remains known today as Javelle water. A short while later, Antoine-Germain Labarraque replaced the expensive potassium hydroxide with caustic soda, resulting in what was probably the first use of sodium hypochlorite as bleach.

Chlorine first began to be used as a disinfectant in the late 1800s, early 1900s. Liquid bleach, sodium hypochlorite, came into widespread use in the 1930s and today it is the most widely used of all the chlorinated bleaches.

Hypochlorite solutions were used for the treatment of open wounds during World War I and led to the use of onsite generation of hypochlorite in hospitals. These disappeared out of favour until the 1990s, which saw a great surge in the interest of onsite generation of chlorine. These onsite generators provide a solution containing only 0.8% chlorine, which is non-hazardous, however hazardous hydrogen gas is produced as a by-product. Onsite generation is also quite inefficient compared with bulk production because of associated electricity costs.

Dry calcium hypochlorite appeared on the US market in 1928. This bleaching

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agent contains up to 70% active chlorine and is also known as high-test hypochlorite (HTH). It is available in a variety of forms including powder, granules, briquettes and tablets. Calcium hypochlorite systems tend to be used for small water treatment plants and well systems. Calcium hypochlorite has a very strong oxidising potential and consequently is very dangerous to store and use. Calcium hypochlorite dissolved in water generates 2 mols of hypochlorous acid for every 1 mol of calcium hypochlorite.

Chlorine as a disinfectant

Not all chlorine species are equally effective as disinfectants. Many studies have explored the mechanism of chlorine disinfection and although it is not possible to precisely explain how each particular chlorine species works, current theory states that inactivation occurs by means of one or more of the following mechanisms: inactivation of the key enzymes, disruption of nucleic acids rendering them non-functional and oxidative damage to cell walls or other vital cell components. For each of the mechanisms above, the effectiveness of each disinfecting agent is a function of both its rate of diffusion through the cell wall and its reactivity with the cell wall, proteins and nucleic acid.

Hypochlorous acid (HOCL) is the most effective disinfectant in the chlorine family available in dilute solution. It is suggested that HOCL is 80 to 120 times more efficacious than sodium hypochlorite. Owing to the fact that HOCL has no charge and has a relatively low molecular weight, it is better than the other chlorine-based disinfectants at penetrating the cell walls. It also reacts more rapidly than other chlorine-based disinfectants to oxidation reactions with organic matter, i.e. the critical components of microbial cells. Conversely, the hypochlorite ion is a relatively poor disinfectant because of its inability to diffuse through the cell wall. Since it is negatively charged, it is electrostatically repelled from the cell walls, which are also negatively charged. It is much larger in size than an HOCL molecule so it also diffuses more slowly.

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Chlorine chemistry

Chlorine is added to water in one of three forms: elemental chlorine (chlorine gas), sodium hypochlorite solution or calcium hypochlorite powder (high-test hypochlorite). Chlorine gas reacts rapidly with water to form two compounds: hypochlorous acid (HOCI) and hydrochloric acid (HCI).

$$\text{Cl}_2$$
 + H_2O \leftrightarrow HOCl + HCl chlorine water hydrochloric hypochlorous acid hydrochloric acid acid

HOCl is a weak acid that further dissociates into the hydrogen ion (H+) and hypochlorite ion (OCl-) according to the following equation:

These three species exist in an equilibrium that is both pH and temperature dependent; the sum of these is referred to as the total available chlorine. At 25 °C and a pH of 7.5, half of the total chlorine is present as HOCl and the other half as OCl-. The dissociated hypochlorite ion (OCl-) predominates at higher pH values, above 7.5 pH, whilst the undissociated hypochlorous acid (HOCl) predominates at lower pH values. At pH 5, nearly all the chlorine is present as HOCl, while a pH value of 10 drives nearly all the chlorine to be present as OCl-.

In a sodium hypochlorite solution that normally sits at a pH of 11–13, all available chlorine is in a form of hypochlorite ions, which as previously discussed is far less efficacious than hypochlorous acid. Until recently, it has not been possible to create hypochlorous acid in a stable solution with a usable shelf life.

Hypochlorous acid generated from dissolving dry calcium hypochlorite has a shelf life of approximately four hours and therefore has not been suitable for use

Poorly produced HCIO disinfectant has an excess concentrations of hypochlorite ions as well as free chlorine gas. In effect, it is bleach, not hypochlorous acid...with bleach's odor, increased toxicity and reduced effectiveness.

Our disinfectant is produced in a manner not to have these issues, and is FDA registered as an effective disinfectin agent, yet, at the same time, is considered to be a "food-safe" ingredient.

Plus, because it is a naturally-occurring chemical that is at the heart of human active immunity, it is not recognized as a foreign chemical, so it does not ellucidate allergic reactions.

As the only disinfectant compound that is approved for use in atmospheric fogging of occupied spaces, iinvestigations are actually underway to determine its potential effectiveness if used as an inhalent! ingredient!

Our disinfectant has a stable shelf life of a yeat, though exposure to strong UV light affects its stability...hence, the caution situate disinfectant tunnels away from direct sunlight.

in pharmaceutical or healthcare environments. Advances in chlorine chemistry have made it possible for contamination control products manufacturer Contec Inc. to stabilise a solution based on calcium hypochlorite at a pH of 3.5 to 5.5, so all available chlorine is in the form of hypochlorous acid as a ready-to-use product with a shelf life of 18 months.

Stabilised hypochlorous acid efficacy

If the science was correct, this hypochlorous acid-based disinfectant should be more efficacious and faster acting than the equivalent sodium hypochlorite product. Contec's solution of 2,000 ppm hypochlorous acid was therefore tested against the standard EN panel of tests for disinfectant efficacy; the table (top of page) shows a summary of these results.

Complete kill against spores was achieved in both clean and dirty conditions against a modified EN 13697 surface test in 1 minute. This is a significant increase in both log reduction achieved and kill rate over sodium hypochlorite. Various micro-organisms were tested, including a particular resistant house isolate, which was typed as P. glucanolyticus. Test work was also repeated against the newest version of EN 1650^6 for fungi and moulds, which has a requirement for >75% of the A niger (now A brasiliensis) spores to be in the form of spiny spores, which are more resistant.

It is not sufficient though for a cleanroom disinfectant to only have powerful activity, as invariably this activity comes at a cost. Either the product is unpleasant for operators to handle because of smell or toxicity or powerful sporicides very often require specialised PPE or costly disposal consideration. Hypochlorous acid at low concentrations is non-hazardous and requires no specialised disposal process or operators to wear any PPE other than standard cleanroom gloves.

Very often, fast-acting and efficacious sporicides are detrimental to the

Our disinfectant is the best of all worlds: At 200ppm, it is twice the level FDA says is adequate to "kill" coronavirus, but is a level that is non-toxice to adults, babies, pets...with little or no odor, taste or residues or irritiation to eyes, skin, mouth or even open wounds

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environment they are used in. At concentrations of 2,000 ppm, hypochlorous acid is non-corrosive, so when used in a controlled manner will be compatible with cleanroom materials. Although not residue free, as hypochlorous acid does leave a very low level of calcium salt on the surface — 1,200 ppm per 100 ml on a residue on evaporation test — it compares favourably with other well-used disinfectants such as quaternary ammonium compounds that give results of 4,500 ppm per 100 ml and 21,000 ppm for hypochlorite solutions.

Our disinfectant mfr claims there's no residue after use

To conclude, it would seem that stabilised hypochlorous acid challenges some of the commonly held beliefs about chlorine disinfection as it meets most, if not all, of the ideal cleanroom disinfectant functional requirements.

References

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