

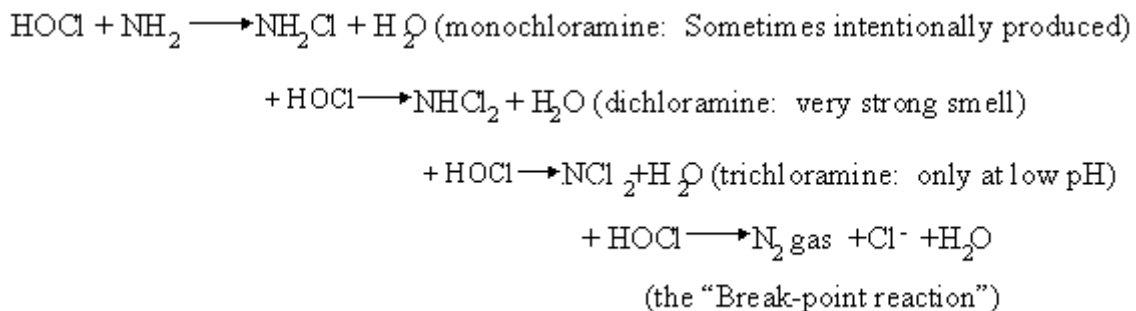
DISINFECTANT BY-PRODUCTS

All chemical disinfectants are poisons of some kind, and the most important are oxidizers like chlorine and ozone. Whenever oxidizers are used, they "attack" all sorts of other things in the water besides micro-organisms, producing a variety of unwanted chemical byproducts. Many of them are carcinogenic or otherwise toxic, and their nearly universal occurrence has made them very prominent in recent news reports. This is in spite of the fact that most of them are obscure chemicals with unpronounceable names, and they occur in such faint traces (parts per billion, ppb, and even less) that their importance as contaminants is difficult for many people to understand. This Bulletin will lay them out for you, as a reference.

BYPRODUCTS OF CHLORINE DISINFECTION:

Chlorine is the most commonly used water disinfectant, and organic compounds are the most common oxidizable contaminants, so most of the disinfection by-products (DBPs) identified so far are chlorinated organics. Ozone is powerful enough to produce free chlorine from chloride ion, and if the water contains bromide ion, either free chlorine or ozone can oxidize it to free bromine, and both can then participate in the reactions with organics. Most organic material in water has a biological origin-it is either cellular fragments of recently-dead micro-organisms and plants, or "color" molecules of the brownish tannin-lignin-humus complex-like tea-that leaches out of dead vegetation. The latter is almost pure "carbohydrate," containing only carbon, hydrogen, and oxygen. But the recently-dead matter includes proteins, amino acids and nucleic acids, which contain lots of nitrogen atoms that react freely with chlorine. Many surface water supplies may also have significant levels of nitrogenous fish and animal waste materials such as ammonia and urea. These contaminants cause a lot of trouble when chlorinated, because, at best, they smell and taste terrible, and at worst, they may cause cancer or miscarriages.

CHLORAMINES: When ammonia (NH₃) or nitrogen-containing organics are in contact with aqueous chlorine (HOCl, hypochlorous acid), "chloramines" are produced. If the chlorine level is maintained, all amine-nitrogens will have their hydrogen atoms replaced with chlorine, as long as there are any to replace. The last reaction in the sequence produces harmless nitrogen gas, which bubbles off to join the other 80% of our atmosphere. This is shown below, in steps, using the simplest example, ammonia:



Even though all of these chloramines are toxic and offensive to some degree, the first reaction is intentionally produced in about 25% of U.S. water supplies. This is usually done by injecting ammonia as the finished water leaves the water-works, converting the free chlorine residual that accomplished disinfection earlier into monochloramine. They do that because monochloramine still retains about 5% of free chlorine's disinfection power, which is enough to inhibit bacterial regrowth in the distribution system, but it is not powerful enough to continue producing toxic chlorinated organics, which free chlorine would do if it were still present. But monochloramine lasts a lot longer in the mains than free chlorine, so it is often a good trade-off. The surface water supplies used by many of the largest cities contain so much organic matter that it is more economical to meet the THM standard (which see, below) by limiting the extent of chlorination than by using more thorough treatment to remove the organic precursors first. And these largest municipal systems are exactly the ones that need a disinfectant residual to last the longest in the mains, so "chloramination" makes sense for them.

The last reaction in the sequence given above is critically important. It is called the "break-point reaction" because it represents the destruction or "breaking" of the last of the oxidizable material in the water, called the oxidant demand or chlorine demand, leaving behind a "residual" of "free available chlorine" (FAC) to do the actual disinfection. Disinfection cannot proceed until the oxidant demand has been destroyed. Thus, when testing for chlorine with a chemical test kit, it is critically important to be able to distinguish between FAC (which disinfects) and "combined chlorine" (which does not disinfect). If the purpose of the test is to assess taste & odor, use the "Total Chlorine Test," which includes FAC and all of the many kinds of combined chlorine that may be present. If the purpose of the test is to assess disinfection and safety, test specifically for FAC, or free chlorine.

HALOGENATED ORGANICS: When organic matter is in contact with free chlorine, a large variety of oxidized and chlorinated organic compounds is produced. The most common are one- and two-carbon fragments of larger molecules with a number of chlorine and/or bromine atoms attached, exemplified by tri-chloro-methane or chloroform, CHCl_3 , the predominant THM or trihalomethane. A generation ago, when these contaminants were first discovered in drinking water, concentrations of several hundred ppb were common. Now, after many years of actively avoiding THM production, most water-works supply tap water with less than 20 ppb. THMs have been considered probable human carcinogens (kidney, liver, bladder cancers) and have been regulated in drinking water for many years with a mandatory Maximum Contaminant Level (MCL) of 0.10 ppm. However, the U.S. EPA recently proposed to relax that, to 0.30 ppm, because new data has finally established that there is a carcinogenic threshold level for these compounds, and 0.30 ppm is safe. On the other hand, other new data from other sources has now implicated THM levels as low as 0.08 ppm (80 ppb) as a cause of miscarriages.

Next in prominence after THMs are the halogenated acetic acids or HAAs, the halogenated aceto-nitriles or HANs, and the halogenated ketones or HKs, most of which are made from two-carbon fragments. They are found in chlorinated waters at levels one-third to one-half of the THM level. If and when they are ever regulated explicitly, it is expected that they will receive MCLs in the 30-80 ppb range.

Probably the most recognizable chlorinated organics are the chlorophenols, a chemical family with 6-carbon rings (benzene rings) with one or more -OH groups attached, plus one or more chlorine atoms. They have moderate toxicity, but their main offense is an extremely powerful "medicinal" or "iodine-like" taste & odor. The worst is 2,4-dichlorophenol, with a taste & odor threshold of only a few parts per trillion (ppt). Pentachlorophenol is probably the most well known of the group. It is used as an insecticide to kill termites and as a fungicide to prevent wood rot in telephone poles, etc. All of the chlorophenols are easy to oxidize to oblivion-just add more chlorine-and that signals their true importance: their characteristic stink occurs only when disinfection has been lacking and/or the remaining chlorine residual is too weak to do anything. The presence of chlorophenol T&O indicates that the water is unprotected and that more chlorine is needed. This problem actually occurs more often in systems using ozone or chlorine dioxide for disinfection than in those using plain chlorine. Their source in water is usually chlorination of the brownish "color" molecules, which produces many "phenolic" fragments in addition to the many one- and two-carbon fragments mentioned earlier. Reactive phenols can also leach out of certain plastics that may improperly find their way into the beverage circuit of commercial equipment such as coffee makers and vending machines. If the equipment is protected with a carbon filter to control T&O, excessive flow rate or continuous use might occasionally be able to strain the filter's chlorine-reducing efficiency. If only a few parts per quadrillion (ppq!) of chlorine get past the filter and are available to react with a few ppq of a phenol, they can produce a few ppt of a chlorophenol that tastes and smells terrible. The remedy for this kind of T&O problem is to avoid using phenolic plastics in water-using equipment. The remedy for chlorophenol odor in an ordinary water supply is to enhance the disinfection process so that any phenols are destroyed, along with the rest of the oxidant demand.

In addition to the above "families" of related chloro-organic compounds, there are also several isolated, individual byproducts that bear mentioning. These include chloropicrin, also called nitrochloroform, and cyanogen chloride, both of which were used in chemical warfare; and chloral hydrate, once known as "Mickey Finn" knockout drops. Of course, their concentrations in chlorinated water are much too low to cause those effects, but they certainly illustrate the variety and notoriety of the group.

BYPRODUCTS OF CHLORINE DIOXIDE DISINFECTION

Surprise, there are hardly any chloro-organics produced by the action of chlorine dioxide on the organics in drinking water. However, its main breakdown product, chlorite ion, ClO_2^- , and its main precursor, chlorate ion, ClO_3^- , are both toxic, causing oxidation of the iron atoms in hemoglobin so that the red blood cells fail to distribute oxygen to the tissues effectively. This is a potentially deadly condition called "methemoglobinemia" (from meta, Greek for "beside" or "other"), and it is also the toxicologic mechanism of poisoning by cyanide, carbon monoxide, and nitrite salts.

BYPRODUCTS OF OZONE DISINFECTION

First, ozonation can produce all of the chlorinated organics that chlorination produces, because ozone oxidizes chloride and bromide ions to free chlorine and bromine. That includes the bromate ion, BrO_3^- , (similar to chlorate, above), which forms when bromine is involved and the water is alkaline. In addition, a host of other

oxidation products (alcohols, aldehydes, ketones, and organic acids) are readily formed, both with and without any added chlorine or bromine atoms. Formaldehyde (H₂C=O) and glyoxal (O=CH-HC=O) are the main ones, produced by chlorination as well as ozonation. [Oxidation of organic compounds often proceeds in steps, first producing an alcohol (-C-OH) and then oxidizing the alcohol to a ketone or aldehyde (-C=O), and then oxidizing that to an organic acid (-C=O-OH).] A couple of complex organic pesticides are only partially oxidized by ozone, producing new compounds that are more toxic to humans than the original chemical. These are heptachlor epoxide (from heptachlor) and aldicarb sulfoxide and aldicarb sulfone (from aldicarb).

Another unusual ozonation byproduct to consider is the huge variety of larger fragments of natural organics that don't have names, but simply provide ready nutrition to micro-organisms. The tannin-lignin-humus complex that creates "color" in water normally takes many centuries to be broken down by bacteria, but "pre-digestion" by ozone often leads to runaway bacterial re-growth in the water mains if and when the disinfectant residual dissipates. Therefore, water systems using ozone for disinfection often include large granular activated carbon beds, where intentional bacterial growth consumes so much of the organic "soup" that subsequent regrowth in the mains is greatly reduced. This is called Bacteriological Activated Carbon or BAC treatment.

Disinfection By-Products (DBPs)

Inorganics

- Chloramines
- Dichloramine
- Ammonia
- Bromate ion
- Chlorite ion
- Monochloramine
- Chlorate ion
- Trichloramine

Haloacetic acids (HAAs)

- Monochloroacetic acid
- Trichloroacetic acid
- Dibromoacetic acid
- Monobromoacetic acid
- Dichloroacetic acid
- Bromochloroacetic acid

Haloacetonitriles (HANs)

- Monochloroacetonitrile
- Trichloroacetonitrile
- Dibromoacetonitrile

Haloketones (HKs)

- 1,1-Dichloropropanone
- 1,1,1-Trichloropropanone

Trihalomethanes (THMs)

- Chloroform
- Dibromochloromethane
- Bromoform
- Bromodichloromethane

Chlorophenols

- 2,4-Dichlorophenol
- 2,6-Dichlorophenol
- 2,4,6-Trichlorophenol

Aldehydes

- Formaldehyde
- C₂-C₁₄ Aldehydes

- Monobromoacetonitrile
- Dichloroacetonitrile
- Bromochloroacetonitrile

- Glyoxal
- Methyl glyoxal
-

Others

- Chloropicrin
- Cyanogen chloride
- Chloral
- Chloral hydrate
- Chlorinated furanones (MX)
- 2,2-Dichloropropanoic acid
- 3,3-Dichloropropanoic acid
- 2,3,3-Trichloropropenoic acid
- Dichloropropanedioic acid

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