

Experiments in Removing Chlorine and Chloramine From Brewing Water

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1.0 Introduction

Chlorine is well known as a disinfectant of municipal water supplies and swimming pools. Brewers have long been aware of the detrimental effects of chlorine on beer brewed with water containing it and know that it can be removed by the traditional methods of allowing the water to stand, by aerating it, by boiling it or by passing it through an activated carbon filter. Recently attention within the brewing community has been drawn to the fact that an ever increasing number of public water suppliers are supplementing or replacing the familiar free chlorine with chloramines which are compounds of chlorine and nitrogen created when water is dosed with chlorine in the usual way and then subsequently with ammonia. Chloramines are less familiar to brewers and are commonly thought to be virtually impossible to remove from water other than by activated carbon filtration. This is not entirely so. While chloramine is more stubborn than chlorine it is nevertheless true that the traditional techniques used for free chlorine reduction can be used for chloramine as well though the required treatment times with chloramine are sufficiently longer that the reader may not consider the traditional methods practical.

The author first began to suspect that boiling and aeration might remove chloramine from water in the spring of 1998 and few simple experiments confirmed the suspicion. This finding was posted to the Home Brewers Digest in an article entitled "Chloramine Heresies" (Ref. 1.). Since then, more elaborate experiments have been performed and it is the purpose of this article to report on some of the findings of those experiments though the investigation is far from complete. As the brewer's sole interest in chloramine is in removing it from his water the experiments were all directed towards the goal of finding effective means of doing this. Several methods were tried including the traditional ones and some chemical ones. Experiments were run on home brewing volumes (10 gallons) of standardized water which we chloraminated ourselves and on samples from two municipal suppliers. We determined the rate at which chloramine (and free chlorine as well in most cases) left the water and express this rate by the "half life" which is the number of hours required for the chloramine level to be reduced by half. Hundreds of chlorine and chloramine concentration measurements were made over time as the various treatments were applied. Half lives were determined from this concentration vs. time data. Perhaps the most important conclusions from the test data are that chloramine is more difficult to remove with the traditional methods and its behavior is somewhat unpredictable. The half lives of chloramine in the three water types tested were dramatically different in the most basic (undisturbed standing) test and the boiling test. This is related to the complexities of chlorine/ammonia chemistry which depends on pH, temperature, relative chlorine and ammonia concentration, the passage of time and the presence of minerals normally found in drinking water. Its significance is that the reader contemplating use of one of the methods we tried must verify its effectiveness on his water. Fortunately, chlorine/chloramine testing is very easy to do and there are many inexpensive test kits on the market. Using one of these the brewer can check whether the treatment he has chosen has eliminated chloramine and even estimate the half life of chlorine and chloramine in his water supply if he wants to. Instructions for doing this are given later in the article.

The data show that all chlorine (free and chloramine) can be removed from water by boiling, aeration or standing though very long times (relative to those for free chlorine) may be required. The easiest and fastest method of chloramine (and chlorine) removal seems to be the simple addition of Campden tablets to the water. One tablet will treat 20 gallons in most cases but we encourage the brewer to test here too. The idea of using this class of chemicals for chlorine reduction is hardly novel (most water treatment plants stock them for this purpose as do aquarists - also see Ref. 2.) but we believe that our suggestion that Campden tablets are effective against chloramine may be new, at least on this side of the Atlantic. We have had private communications to the effect that Campden tablets are currently being recommended for chloramine reduction among British home brewers.

2.0 A Little History

Chlorine was first used experimentally for disinfection of a municipal water supply in Louisville, Kentucky in 1896. The first permanent installation of chlorination equipment in a water treatment plant in this country was made in 1908 and it has been in continuous use since then (Ref3.). Chlorination is simple, effective, relatively safe and inexpensive. Its efficacy comes from the strong oxidizing¹ potential of the hypochlorous acid molecule formed when either chlorine gas or salts, such as sodium hypochlorite, are dissolved in water at modestly low pH. Chlorine oxidizes not only bacteria and viruses but other substances found in water as well. Plants contain phenols and plant matter finds its way into surface waters so that such waters, when chlorinated, may have the flavors and aromas of chlorophenols which are regarded no more highly in the water industry than among brewers. If, after the chlorine has done its job of killing pathogenic (and other) organisms at the water plant, it can be converted to a less active form it can still maintain some of its bacteriostatic power but will not be active enough to form chlorophenols during its travel through the distribution mains to the customer. Injecting ammonia into water accomplishes this and was first done for purposes of flavor improvement in 1926 at Greenville, Tennessee where the water had objectionable qualities from the presence of phenols (Ref. 4.) It's continued use today is partly motivated by taste improvement but much more strongly by the desire to limit chlorine reaction with other organics from decaying vegetation which are often found in surface water. These decay products (mostly humic and fulvic acids) combine with chlorine to produce a family of chemicals called *trihalomethanes* (THMs) which are thought to be carcinogenic. Today's federal and state drinking water regulations regulate allowable THM levels quite strictly. Because of this more and more water treatment plants in the USA limit the exposure of the water to chlorine to the minimum necessary to kill target organisms. The residual chlorine is then converted to less active chloramine by addition of ammonia. It is estimated that 25% of the larger and perhaps 5% of smaller (personal communication) water treatment plants in the US use chloramination today as compared to about 2.6% of plants surveyed in 1963 (Ref. 8.)

As water suppliers have converted to this new method they have notified their customers of this fact, as well they should, for it is essential that aquarists, for example, be aware that their water source is chloraminated. This is because they traditionally use sodium thiosulfate for chlorine removal. In the presence of chloramine, reduction by thiosulfate releases ammonium ion which is converted to ammonia as aquarium pH climbs and ammonia is toxic to fish. Compare to the brewing situation in which pH is continuously reduced through the mash and fermentation. The ammonium ion stays as the ion and is an additional source of nitrogen for the yeast. Thus thiosulfate and the related pyrosulfites, which we prefer, are fine for brewing and we will have more to say on this later.

¹. "Oxidizing" here is used in its broader chemical sense in which it refers to the taking of an electron or electrons from the substance being oxidized. Oxygen is certainly capable of doing this but it is only one member of a larger class of substances referred to as "oxidizing agents".

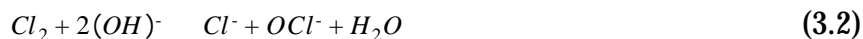
The use of chloramines has led to anxiety (Ref 5.) in the aquarium hobby and the water authorities' publicity information often contains statements like "Fish tank owners...will have to make sure they have appropriate carbon filtration equipment or use water treatment products that neutralize chloramine..." and "Allowing water to sit exposed to the atmosphere is not an effective means of removing chloramines." (Ref 6.). Statements like this are seen by brewers and give them the impression that there is something special about chloramines such that the traditional simple methods of chlorine amelioration are no longer effective.

3.0 Why and How Chloramines are Introduced into Tap Water

We mentioned in the previous section that it is the oxidizing property of hypochlorous acid that results in the destruction of bacteria, viruses and protozoa in treated water. When chlorine is mixed with water the following reaction takes place



The reaction is shown here as it occurs at a low pH which means that molecules, $HOCl$, of the acid will be formed rather than the hypochlorite ion which is formed at higher pH



The two forms are continuously interchanging as



with the concentration (number of molecules) of OCl^- , symbolized by $[OCl^-]$, being related to the concentration (number of molecules) of $HOCl$, symbolized $[HOCl]$, by

$$[OCl^-] = 10^{(pH - 7.6)}[HOCl] \quad (3.4)$$

Thus the concentration of the two is about equal at pH 7.6 (the actual value is dependent on temperature) with OCl^- being 100 times more prevalent than $HOCl$ at pH 9.6 and the reverse being true at pH 5.6. Both species are oxidizers but $HOCl$ is the better one with an oxidation potential (the means by which strength is measured) of 1.611 volts as compared to 0.841 volts for OCl^- . Further, $HOCl$ is uncharged so that it is better able to penetrate the negatively charged slime coating on the target organisms (death is believed to be caused by disruption of various internal enzyme systems). Thus, for most effective killing action the pH of water being treated should be kept low. pH is controlled at treatment plants not only to insure good killing action from chlorine but to prevent the water from occluding (pH too high) or corroding (pH too low) the distribution system. While typical distribution pH's are not optimum for maximizing the killing power of hypochlorite they are usually less than 7.6 and thus favor $HOCl$.

Effectiveness of disinfection is measured in “log inactivation” units. One log unit means 90% of the organisms are inactivated, 2 log units means 99%, 3 log units means 99.9% and so on. Various federal and local agencies specify the log inactivation ratios required of a treatment plant. The treatment plant insures that the regulatory requirements are met by implementing an available chlorine concentration and exposure time (referred to as “C times T” or just “CxT”) which will do the required job on the specified organism. CxT depends on chlorine concentration and pH. Representative CxT values are given in the table for chlorine, ozone and chloramine. Ozone is seen to be the most effective disinfectant and chloramine the least. We will be commenting on the significance of that in subsequent sections.

Table 1: USEPA Representative CxT Values (Ref. 10.)

Organism	Log Inactivation	Disinfectant	pH	CxT 50°F	CxT 77°F
Giardia	3	Free Chlorine	6	87 mg-min/L	29 mg-min/L
Giardia	3	Free Chlorine	7	124	41
Giardia	3	Free Chlorine	8	182	61
Giardia	3	Free Chlorine	9	265	88
Giardia	3	Ozone	6-9	1.4	11
Giardia	3	Chloramine	6-9	1850	750
Virus	2	Free Chlorine	6-9	3	1
Virus	3	Free Chlorine	6-9	4	1
Virus	4	Free Chlorine	6-9	6	2
Virus	2	Ozone	6-9	.5	.15
Virus	3	Ozone	6-9	.8	.25
Virus	4	Ozone	6-9	1.0	.3
Virus	2	Chloramine	6-9	643	214
Virus	3	Chloramine	6-9	1067	356
Virus	4	Chloramine	6-9	1491	497

We also noted in Section 2.0 that bacterial enzymes are not the only things that can be oxidized by hypochlorous acid. Other organics which are found in the water as a consequence of things, plant and animal, which live in it, die in it, fall into it or over which it washes can be oxidized by chlorine and this has both positive and negative implications depending on the substances. Plant material, for example, contains phenol compounds and, as brewers well know, these can be oxidized by chlorine to chlorphenols which have extremely low flavor detection thresholds. The potential for their formation is the reason why we try to remove chlorine from our water in the first place. They can be produced at the water treatment plant as well and the author has seen puzzled queries as to why beers made with thoroughly dechlorinated water still present chlorphenolic flavors. The answer is that the chlorphenols were already there!

Another thing which is already there is ammonia - the urea in the excreta of fish, for example, produce it upon decomposition. When ammonia meets chlorine, as we shall see, chloramines are formed. Thus the nation's drinking water contained chloramines before ever they were introduced intentionally.

When chlorine oxidizes plant derived humic and fulvic acids the products may contain trihalomethanes (THMs) which are of great concern in the water treatment industry today. As the name implies these are compounds in which three of the hydrogens in methane, CH_4 , have been substituted by a halogen (fluorine, chlorine, bromine, iodine). There are 4 THMs with which the regulators are concerned and the best known of these is chloroform, $HCCl_3$. The others are bromodichloromethane, $BrCHCl_2$, dibromochloromethane, Br_2CHCl and bromoform, $HCB r_3$. While it has not been firmly established, evidence is mounting that THMs are carcinogenic and, as a consequence of this, the MCL (maximum contaminant level) for THMs will be set to around 100 ppb in the near future.

The positive result of oxidation by chloramine is that many oxidation products are not bad tasting or smelling or carcinogenic. Thus chlorine is effective in improving the appeal of water in many cases in addition to rendering it safer by the destruction of pathogenic bacteria. Nevertheless, today the emphasis is on the THM rule and plant managers spend a great deal of effort in striving to meet it. There are a couple of ways in which this can be done

Oxidize organics with oxidizing agents other than chlorine: Potassium permanganate is an effective oxidizer which is used in limited quantities in some plants. It's expensive and the manganese produced must be removed (which it is in the course of normal flocculation treatment). Installation of ozone treatment equipment is becoming more common. Ozone is made from air by exposure to intense ultraviolet light so that the raw material is free. Nevertheless, the capital and operating costs of ozonation equipment are large. As shown in the CxT table of the previous section, ozone is a very efficient disinfectant as well as a good oxidizer for phenols, etc.

Remove oxidizable organics prior to chlorination: In this approach the flocculated water is polish filtered through a filter medium which contains activated carbon particles. These adsorb a large portion of THM precursors as well as phenols and other organics. Thus chlorphenols and THMs are not formed when subsequent chlorination is performed. The carbon beds can be backwashed and ultimately regenerated.

Limit chlorine exposure to the minimum CxT required to meet the Total Coliforms requirement: In this approach, often used in conjunction with one or both of the other two, post finish filtration water is chlorinated to an appropriate C and then stored in a clearwell for an appropriate T. As the water leaves the clearwell to enter the distribution system ammonia is injected. This results in the formation of the chloramines, H_2NCl , $HNCl_2$, and NCl_3 . The chloramines are much less active than hypochlorous acid having but 1 ten thousandth (according to Ref. 11.) of its effectiveness as a chlorinating agent though the CxT table shows it to be perhaps 200 times less effective. Whichever is closer to the truth, the reduced capability is sufficient because, in the first place, at the point in the process where chloramine is formed, the water has been exposed to sufficient CxT of whichever disinfectant has been used to render it safe and second, not all the chlorine is converted i.e. the water which enters distribution has both residual chlorine and chloramine content. The chloramines are also less active in THM formation than the equivalent amount of chlorine. The net result is that the dose of free chlorine plus chloramine is sufficiently high to maintain bacteriostasis during the water's trip from the plant to the consumer but low enough that insignificant additional THMs are formed in that time. Thus the consumer's tap water meets both the Total Coliforms requirement and the THM requirements of the cognizant regulatory agencies. An additional benefit is that monochloramine is less odoriferous than free chlorine and has a higher taste threshold meaning that the tap water tastes and smells better.

4.0 Properties of Chloramines

Monochloramine is formed by the oxidation of (removal of a hydrogen atom and in particular its electron from) ammonia by hypochlorous acid:



Monochloramine has two more hydrogens to give and can, therefore, be oxidized in two further steps



to, respectively dichloramine and nitrogen trichloride.

The rates of formation of monochloramine are much greater than those for dichloramine and nitrogen trichloride but all depend on the initial chlorine to ammonia ratio, temperature and pH. Thus it is possible to control the relative amounts of the three chloramines to some extent. As a general comment, the higher the pH the more prevalent monochloramine will be though the balance at a given pH will shift over time as some monochloramine converts to dichloramine. At pH 9 90 - 100% of total chloramine chlorine is monochloramine. Conversely at pH 5 60 - 90% is dichloramine. In both cases the first number is an initial value and the second is reached as time passes.

Trichloramine is very volatile and is easily swept out of water. Dichloramine is also quite volatile but monochloramine is not. According to Ref. 12. aeration is ineffective in removing monochloramine and in the same place it is stated that free chlorine is "nonvolatile" where calcium or sodium are present (as they are in most waters). From this we conclude that it is usually difficult to remove free chlorine by aeration under any circumstances and difficult to remove chloramine where pH is high enough (say greater than 7) that monochloramine is dominant. This suggests pH reduction as a strategy for chloramine removal and we will discuss this further in Section 5.6.3.

Table 2 lists some of the properties of the three chloramines. Note that dichloramine and nitrogen trichloride are detectable, both in odor and taste, at appreciably lower levels than monochloramine. For this reason, water processing plants operate so as to produce water that is relatively high in this form and low in the other two. Their intent coupled with the high volatility of dichloramine and nitrogen trichloride makes it clear that most of the chloramine you will see in your tap water is monochloramine.

Table 2: Some Properties of Chloramines

	Odor Threshold	Taste Threshold	State (at room temp)	Volatility
Monochloramine	0.48	0.65	Yellow Liquid	Low
Dichloramine	0.13	0.15		High
Nitrogen Trichloride	0.02	0.02	Yellow oil/rhombic crystals	Very High

5.0 Experiments in Removing Chlorine and Chloramine

In this section we report the methods and results of the experiments in which we removed chlorine and chloramine from water using several treatment schemes.

5.1 Basic Experimental Procedure

In all our tests a 10 gallon volume of chloraminated water was placed in a 15 gallon Vollrath stockpot which is 16.25 inch in diameter. The surface area is thus 207 square inches and the area to volume ratio 20.7 square inches per gallon. In the simplest tests this volume of water was allowed to stand undisturbed. In other cases the water was circulated with a small pump, circulated and simultaneously aerated with an aquarium pump and aquarium aeration stone or boiled. Where chemical additions were involved, the chemicals were added and thoroughly stirred in with a stainless steel paddle.

Chlorine and chloramine levels were measured periodically with a frequency dictated by the rate at which the levels changed. This means that measurements could be taken as infrequently as twice a day for conditions where the half life is large (standing tests) and every couple of minutes where it is small (boiling tests). All measurements were made with a Hach DR4000 spectrophotometer using DPD chemistry (Hach Catalog 21055-69) for free chlorine and DPD plus potassium iodide (Hach 21056 - 69) for total chlorine. In the latter test, chlorine and chloramine oxidize iodide to iodine and the iodine then oxidizes the DPD to form the color in the same way that chlorine oxidizes it in the free chlorine test. Chloramine is estimated as the difference between the free and total chlorine readings. See Section 6.0 for more detail.

The chemistry/photometer combination was checked against a NIST traceable chlorine primary standard and found to be within 1.5% (0.02 mg/L) for the range over which the vast majority of measurements were taken (below 1.4 mg/L). In fact most were taken in the range where the error was less than the precision of instrument reading (0.01 mg/L). Nevertheless, we call the standard error per reading 0.02 mg/L and, as chloramine estimates involve the difference of 2 readings, use 0.03 mg/L in calculations of error estimates.² The instrument was checked daily against a secondary standard.

Section 6.0 contains information on various other means of measuring chlorine and chloramine, many of which use simple, inexpensive kits.

5.2 Water for Experimentation

The chemistry of ammonia and chlorine is quite complex and, though it is surprising given the current concern within regulatory bodies over disinfection by-products, not fully understood. There are multiple paths that can be followed when chlorine and ammonia are mixed and we earlier mentioned some of the factors which influence the path actually taken. For comparison of treatment methods in our experiments we needed water which contained stable monochloramine at consistent levels. We could not get this from tap water as tap water is not under our control and disinfectant levels vary. We illustrate with a few details concerning the municipal supplies most readily available to the author³: Fairfax City and the Fairfax County Water Authority (FCWA), both operating in northern Virginia. Fairfax City obtains most of its water from neighboring Loudon County which draws it from Goose Creek which feeds into the Potomac River. Loudon County does not chloramine and at times Fairfax City water is chloramine free and thus of no value for our experimentation. When demand increases, Loudon County buys some water from FCWA whose source is the Potomac River. Fairfax City also buys directly from FCWA when circumstances warrant. FCWA chloramines heavily. Their goal at the plant output is 3 - 4 mg/L (virtually all chloramine - free chlorine is typically 0.1 mg/L or less) and, at the consumers tap, at least 2 mg/L chloramine. Fairfax City water can thus contain chloramine. It even does so at times when Fairfax City says they are not connected with FCWA⁴. FCWA water is always high in chloramine but even here the levels vary at the tap due to variations in the amount of chloramine consumed (chlorine and chloramine are converted to chloride ion when they oxidize something) in passing through the distribution system.

². This value represents the approximate root sum square of the errors from two readings each with a standard error of 0.02 mg/L.

³. The author draws his water from a well.

⁴. Presumably this chloramine comes from reaction of ammonia already in the water with the chlorine introduced at the plant.

We did some testing with municipal water from the two sources named in the previous paragraph but most of the experiments were done with synthetic chloraminated water i.e. water we chloraminated ourselves with the intention of establishing a modestly high level of stable chloramine. We chose monochloramine stable water to experiment with so that our results would represent the worst case. The literature suggested and we found empirically that a stable monochloramine concentration could be established in chlorine (and chlorine demand) free water whose pH had been adjusted to near 8 (pH adjustment was accomplished by the addition of slaked lime) by pretreating with an excess of ammonia in the form of ammonium hydroxide and then adding sodium hypochlorite. We diluted 26° Be' ammonium hydroxide 25:1 with deionized water and added 2 mL of this to 10 gallons (38 L) of well water⁵. We then added 0.8 mL of sodium hypochlorite solution (household bleach) which contained 56 mg chlorine per liter (this is said to be 5.6 "trade percent" hypochlorite). This amounts to 1.18 mg/L chlorine and measurement of treated water is typified by 0.07 mg/L free chlorine and 1.09 mg/L chloramine. These readings were stable over time and thus indicate that the chloramine is monochloramine as dichloramine or trichloramine would volatilize rapidly. A high fraction of monochloramine was anticipated because of the excess of ammonia and because of the high pH which favors conversion of dichloramine to monochloramine.

This method of chloraminating water is typical of what would be done in a small (e.g. community well) water treatment facility. These facilities buy chlorine as hypochlorite solution or powder and ammonia as the hydroxide mostly because of safety and shipping considerations. Larger facilities buy chlorine and ammonia as the compressed and liquefied gasses and must take elaborate measures to store and handle them safely.

As it turned out water from the FCWA showed longer chloramine half life than the water we synthesized. FCWA chlorinates as the water enters the clearwell and then ammoniates as it leaves the plant. Fairfax City water showed chloramine with shorter half life than the synthetic water.

⁵. Nominal pretreatment analysis: pH 5.8, Alkalinity 43 ppm as CaCO₃, Calcium Hardness 58 ppm as CaCO₃, Mg Hardness 52 ppm as CaCO₃, Sulfate 38 mg/L, Chloride 7.7 mg/L

5.3 The Concept of Half Life

In the traditional means of removing chlorine and chloramine from water (standing, standing with aeration, standing with circulation and boiling) the chlorine and chloramine leave the water over the course of time and the significant question is, of course, how long one must continue the treatment before the concentration of these volatiles is reduced satisfactorily. In our experiments we are interested in determining the relative rates of departure of chlorine and chloramine and quantifying the relative effectiveness of various treatments. The *half life* lets us both compare relative rates numerically and determine required treatment times. Simply put, the half life is the time it takes for the concentration of, say chloramine, to be reduced to half its value. It doesn't matter what the starting or ending values are and this is one of the best features of half life. At the end of one half life the concentration will be half the starting concentration, at the end of two half lives it will be one quarter, at the end of 3, one eighth and so on. To illustrate this, let us assume that a treatment results in a chloramine half life of 10 hours. Let us assume that a brewer measures the chloramine content of his water prior to a brewing session and finds it is 3.4 mg/L. Call this Water A. At another brewing occasion he measures the initial chloramine concentration at 2.0 mg/L. Call this Water B. The columns of Table 3 indicate the levels of chloramine to be expected at multiples of the half life for both these waters. The table also lists the fraction of chlorine or chloramine left after integer numbers of half lives. These fractions can be used to calculate the number of half lives required for a given reduction. For example, if the brewer confronted with 2 mg/L chloramine wants to reduce it to 0.05 mg/L or less he would compute the fraction remaining after this reduction as $0.05/2 = 0.025$. Consultation of the fraction table shows that a reduction to 0.025 requires between 5 and 6 half lives or 50 - 60 hours if the half life is 10 hours.

Table 3: Example Concentrations for Half Life of 10 hours

Time, hours	Number of Half Lives	Fraction Remaining	Water A Chloramine, mg/L	Water B Chloramine, mg/L
0	0	1.00000	3.40	2.00
10	1	0.50000	1.70	1.00
20	2	0.25000	0.85	0.50
30	3	0.12500	0.425	0.25
40	4	0.06250	0.213	0.125
50	5	0.031250	0.106	0.063
60	6	0.015625	0.053	0.031
70	7	0.007813	0.027	0.016

If more precise values or calculator or computer computation is desired, the formula

$$t = t_{1/2} \frac{\log \frac{C}{C_0}}{\log(0.5)} \quad (5.1)$$

can be used to calculate the required time, t . In this formula C is the desired concentration, C_0 is the initial concentration and $t_{1/2}$ the half life. For our example, C/C_0 is $.05/2 = 0.025$ and the log of this is -1.602 . Dividing this by -0.301 , the log of 0.5 gives 5.32 half lives (between 5 and 6) and multiplying by the half life of 10 hours gives 53.2 hours as the required time.

The concept of half life is valid when the rate at which the volatile substance (chlorine or chloramine) leaves the water is proportional to its concentration in the water and the proportionality is constant over time. When this model for departure of the volatile is valid, a plot of the logarithm of the concentration against time should give a straight line whose slope depends on the rate proportionality. Figure 5.1 shows the logarithm of measured chloramine concentrations obtained as 10 gallons of our synthetic test water was allowed to stand undisturbed for about 118 hours. At the end of that time circulation of the water was begun with a small pump and measurement continued. The straight lines which best fit the two sets of data were determined by the analysis program which made the plots (Wavemetric's IGOR) and these lines are drawn through the data points. It is evident from the figure that the actual measurements follow a straight line quite closely though there are points which do not fall right on the straight line. This is in part because our measurements are not perfect and in part because things may conspire to change the rate at which the volatile leaves the water. Examples of such things are diurnal temperature variations and changes in air circulation near the vessel containing the water.

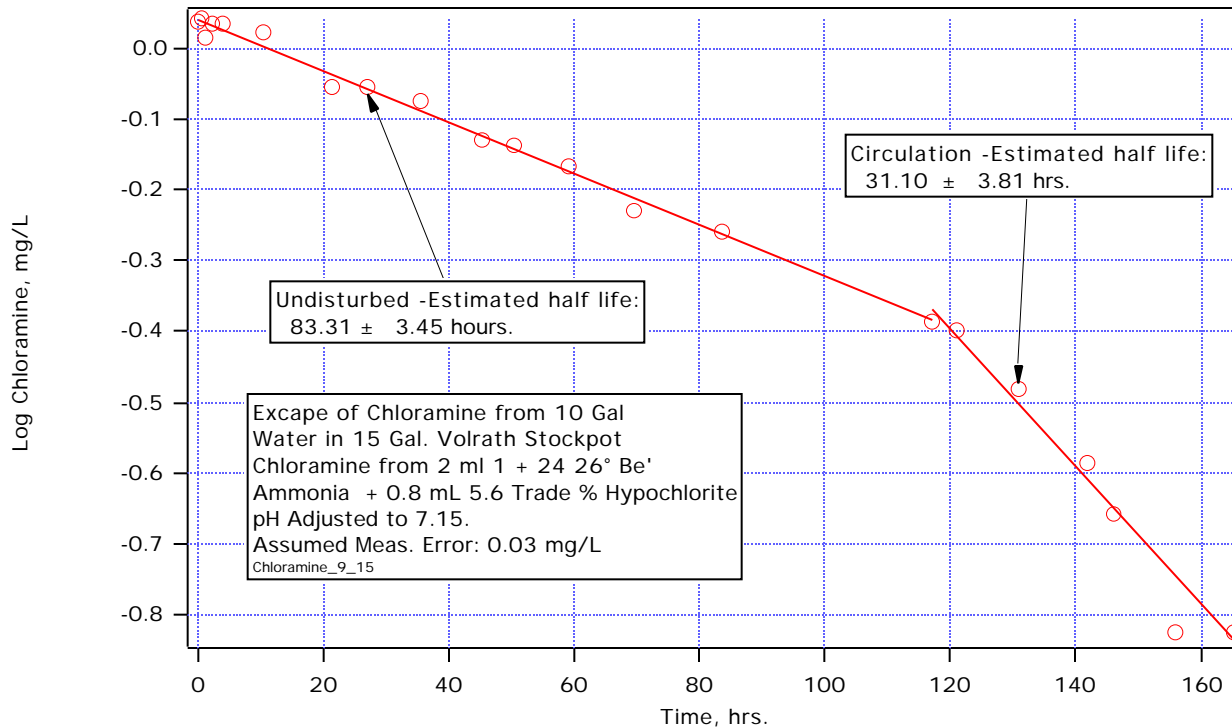


Figure 5.1 Escape of Chloramine From Undisturbed 10 Gallon Volume of Nominal Water. See text for explanation of values in title block.

The half life is obtained from the slope of the line on a logarithmic plot such as Figure 5.1. Some of the mathematical details are given in Section 5.3.2 and a simple method for calculating half life from your own measurements is in Section 5.3.3. The steeper the slope, the shorter the half life. When analysis programs like IGOR compute the slope of the best fitting line they automatically, if given an estimate of the error in the measurements, also calculate the estimated error in the slope. Knowing the error in the estimated slope allows the analyst to calculate the estimated error in the half life computed from the slope and this is the source of the number which appears after the “±” symbol in Figure 5.1 and Table 4.

5.3.1 Things Which Influence Half-Life

The concentration of a volatile substance dissolved in water gives rise to a so called *partial pressure* of that substance in the water. The partial pressure depends on a property of the substance called its *vapor pressure* which increases with temperature. If the air over the water contains some of the volatile in its gaseous form this contributes to the total air pressure proportionately to the ratios of the number of volatile molecules to all other (nitrogen, oxygen...) molecules in air. The rate at which the volatile leaves the water depends on the surface area and the partial pressure difference between the volatile in the water and the volatile in the air. Anything which increases this pressure difference will speed the flow, steepen the slope of the log concentration plot and decrease the half-life. The pressure difference is enhanced if the water side pressure is increased or the air side pressure decreased or both.

Increasing the volatility of the substance increases the water side pressure. Trichloramine (nitrogen trichloride) is more volatile (has a higher vapor pressure at any given temperature) than dichloramine and so has higher partial pressure at a given temperature and concentration and thus leaves water faster than dichloramine, *ceteris paribus*. Dichloramine is more volatile than monochloramine and so monochloramine leaves water more slowly than di- or trichloramine. Free chlorine is more volatile than monochloramine but less so than dichloramine. Vapor pressure increases as temperature goes up and so a temperature increase increases partial pressure on the water side. Increasing the concentration of the volatile in the water increases partial pressure. This occurs locally at the surface when after an interval sufficient to deplete the volatile in the region of the surface the water there is replaced by relatively volatile rich water from the bottom of the vessel as by stirring or circulation with a pump. Either of these operations will increase the speed of departure (decrease half-life) and this is clearly illustrated by the break in the slope shown in Figure 5.1 at the point where circulation was begun.

Lowering of partial pressure on the air side is accomplished by sweeping away the volatile laden air near the surface and replacing it with fresh, volatile free air (or another gas). Draughts in the room (or breezes outdoors) and fans can thus speed removal. Sparging the water with air bubbles or another gas can have the same effect and also offer the increased advantage of offering substantially increased surface area, i.e. the surface of the sparge gas bubbles. Boiling is sparging with steam and, of course, provides the additional benefits of higher temperature

We have not really explained just what it is that leaves the water. The simplest explanation of what happens with free chlorine is that Equation (3.1) is reversed with chlorine being released which escapes to the air. As with most things in chlorine/water chemistry it is not quite that simple. While hypochlorite can be reduced to free chlorine (Ref 16.) it has been suggested that it is actually oxides of chlorine which escape the water. For our purposes the model of Equation (3.1) will do though it does not explain how chlorine can escape if only hypochlorite is present. In consideration of chloramine we assume that it is not ionized and that it behaves, therefore, in fashion similar to an organic volatile such as ethanol when mixed with water. This means that chloramine vapor exists over water in which it is dissolved.

5.3.2 Half Life - Mathematical Details

This Section can be skipped by most readers. The proportionality between rate of departure and concentration is described by a first order linear differential equation which we approximate by

$$\frac{dC(t)}{dt} = -kC(t) \quad (5.2)$$

which reads “the rate of change of concentration C at time t which is the change in C , $C(t)$, in a small time interval, dt , is negative and is proportional to the concentration at time t .” Readers familiar with calculus will pardon this simplification. k , the proportionality constant, depends on the factors discussed in Section 5.3.1. Where

Equation (5.2) holds, the concentration at any time t is given by

$$C(t) = C(0)e^{-t} \quad (5.3)$$

where $C(t)$ represents the concentration at time t after the start of observation and $C(0)$ represents the concentration at the start of observation.

If we take the natural logarithm of both sides of Equation (5.3) we get

$$\ln C(t) = \ln C(0) - t \quad (5.4)$$

This says that the natural logarithm of the concentration would plot as a straight line with slope $-$. Doing the same with logarithms to the base 10 of each side of Equation (5.3) we get

$$\log C(t) = \log C(0) - t \log e \quad (5.5)$$

which also gives a straight line with slope, designated by m

$$m = - \log e = -0.4343 \quad (5.6)$$

Using the properties of logarithms on Equation (5.6) gives

$$\log C(t) - \log C(0) = \log \frac{C(t)}{C(0)} = -mt \quad (5.7)$$

The half life is the time at which $C(t)$ is half $C(0)$ thus solving Equation (5.7) for t when this is so gives the half - life:

$$t_{1/2} = \frac{-\log(0.5)}{m} \quad (5.8)$$

In all our experiments we plotted log concentration vs. time, measured the slope, m , and used this relationship to estimate the half life. Were natural logarithms used the formula would be:

$$t_{1/2} = \frac{-\ln(0.5)}{-} \quad (5.9)$$

Recall that the slope of a natural log plot is $-$.

Earlier in this Section we showed how to calculate remaining chlorine or chloramine for times which are multiples of the half life. For other times the following formula can be used but it is usually sufficient to use multiples of the half-life:

$$C(t) = \frac{C(0)}{2^{t/t_{1/2}}} = C(0)2^{-t/t_{1/2}} \quad (5.10)$$

Equation (5.1) is derived from Equation (5.10) by taking the log (to the base 10) of both sides and solving for t .

One of the big advantages of the half life idea is that makes experimental determination of escape rates much easier. The experimenter only needs enough data to convince himself that an exponential law is being followed. He can then estimate m from the data he has and calculate half life from it. Two data points are the minimum required to do this but good experimental technique requires that more should be taken. As Figure 5.1 shows several points are necessary to convince the analyst that a straight line is being developed. Multiple points show up a change in half life clearly and Figure 5.1 is an excellent example of this. Multiple points also make “outliers” i.e. data points which really don’t belong to the data set clear. Outliers are the nemesis of experimenters but are always present. Finally, the more points considered in estimating the slope, the smaller the standard error associated with that slope. Since the standard error of the half life estimate is

$$t_{1/2} = -\log(0.5) / m \quad (5.11)$$

where $t_{1/2}$ is the standard error in the half life estimate (this is the \pm value in Table 4 and Figure 5.1) and m is the standard error in the slope estimate (this is calculated by the analysis program), we want m as small as possible.

5.3.3 Estimating Half Life Yourself

You can easily estimate the half life of chlorine or chloramine by making a few (as few as 2) measurements of chlorine/chloramine level. To do this, set up your dechlorinating process - say recirculation of water out the bottom of your hot water vessel back to the top using your sparge pump. After everything is set up and has been running for a few minutes, measure the chloramine level (See Section 6.0 for information on test kits and methods). The more accurately you can measure the chloramine level, the more accurate your half life estimate will be. Go do something else for a few hours and then measure again. If there is no detectable change, come back again several hours later. Measurements may need to be taken as far as 12 hours apart.

If a detectable change was seen, note time and new reading and come back the same number of hours later to take another measurement. Keep doing this until you have three or four measurements. Enter these measurements into a spreadsheet listed against the number of hours from the time of the first measurement. Take the log to the base 10 of each measurement and put it into another column. Having done this you can use your spreadsheet’s linear regression program to estimate the slope of the log concentration vs. time data. The half life is found from the slope. In the Excel example of Figure 5.2, the command that finds the slope goes in the cell labeled “Slope” and is “=INDEX(LINEST(C2:C5,A2:A5),1)”. The half life is calculated by dividing minus the log of a half (0.30103) by the slope (ignore both minus signs). The half life is in whatever units have been used to tabulate the readings; hours in the example of Figure 5.2.

Hours	Concentration	Log(conc.)		
0	1.03	0.01283722		
3.95	0.59	-0.229148		
5.667	0.41	-0.3872161		
6.7	0.36	-0.4436975		
	slope <----->	-0.0691221	4.35504976	<--- Half Life

Figure 5.2 Example of Half Life Estimation Using Spreadsheet

If neither a spreadsheet program, nor any other computer based analysis program, is available the logarithms of the concentrations can be calculated with a hand calculator (or even looked up in tables) and plotted manually on graph paper. Draw the straight line through the data point which best fits them i.e. comes closest to them all. Your manual plot will resemble Figure 5.3 in which the straight line was calculated mathematically and is thus the best fit. In a manual plot the slope must be estimated from the grid lines in the plot. The slope is the number of vertical axis units the straight line descends per horizontal axis unit. In Figure 5.3 we see that the straight line descends from -0.05 to -0.15 (-0.1 log units) while running from 1 to 2.5 hours. The slope is thus approximately $-0.1/1.5 = -0.0667$. Compare with the result computed by the spreadsheet.

Obviously readers who have access to programs like IGOR (which made the plot of Figure 5.3) will be able to use their analysis capabilities to fit straight lines and estimate slopes automatically.

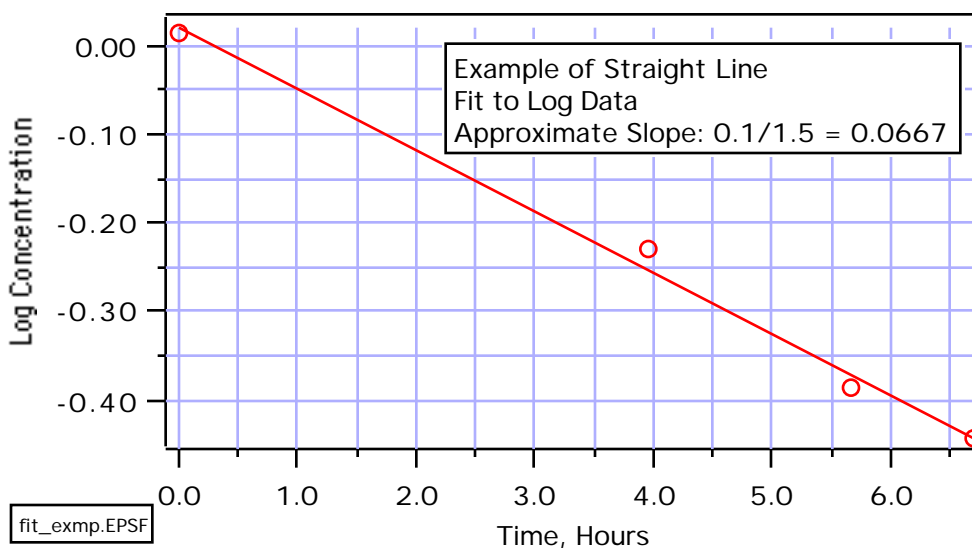


Figure 5.3 Example of Appearance of Best Straight Line Fit to Data of Figure 5.2

5.4 Test Results

Now that the concept of half life is understood we can present the comparative data and this is found in Table 4. We present the data here without comment at this point. Additional details on the individual Treatments and the theory behind them are found in the subsequent sections listed in the "Ref Sec." column of the table.

Table 4: Chlorine and Monochloramine Half Lives - 10 Gallons of Water in 15 Gallon Stockpot

Case	Water	Treatment	Ref Sec.	Free Chlorine Half Life	Mono-chloramine Half Life
1	Synth. ^a	Standing Undisturbed	5.5.1	26.6 ± 1.05 hrs	83.3 ± 3.4 hrs
2	Synth.	Standing with Circulation	5.5.2	4.5 ± 0.3 hrs	31.1 ± 3.8 hrs
3	Synth.	Standing with Circulation and Aeration	5.5.3	3.9 ± 0.7 hrs	30.7 ± 3.1 hrs
4	Synth.	Boiling	5.5.4	1.8 ± 0.06 min ^b	26.6 ± 4.8 min
5	Synth.	Brita Pitcher	5.5.5	7.5% remains ^c	16% remains
6	Synth.	Standing Undisturbed with Bleach Addition	5.6.2	21.8 ± 6.1hrs	1.1 ± 0.08 hrs
7	Synth.	Standing Undisturbed with Acid Addition	5.6.3	37.4 ± 30.1 hrs ^d	20.9 ± 1.1 hrs
8	Synth.	Campden Tablets	5.6.1	< 1 min ^e	< 1 min
9	Fairfax City ^f	Standing Undisturbed	5.5.1	8.49 ± 2.99 hrs	13.30 ± 2.79 hrs
10	FCWA ^g	Standing Undisturbed	5.5.1	41.09 ± 1.08 hrs	155.0 ± 42.0 hrs
11	FCWA	Standing Undisturbed with Bleach Addition	5.6.2	16.81 ± 1.42 ^h hrs	1.34 ± 0.28 ⁱ hrs
12	FCWA	Boiling	5.5.4		10.57 ± 0.38 6.23 ± 1.10 min. ^j

a. Indicates the synthetic water prepared by the author as described in Section 5.2.

b. Estimate based on escape rate between 200° F and boiling. All chlorine had escaped from the sample by the time the boil was reached.

c. In the Brita pitcher test we measured the fraction of chlorine or chloramine remaining in the water after a single pass through the filter.

d. Low levels of free chlorine from the beginning (0.06 mg/L) make accurate estimation of half life difficult

- e. Not measured. When Campden tablets or sodium metabisulfite are used, all chlorine and chloramine are converted to chloride ion in a matter of a couple of minutes.
- f. Water drawn from Goose Creek (runs into Potomac River). No ammonia added. Sometimes blended with water from FCWA Corbalis Plant
- g. Fairfax County Water Authority Corbalis Plant. Water drawn from Potomac River. Heavily ammoniated - nearly all chlorine (3-4 ppm) converted to chloramine.
- h. This was the initial reduction rate for chloramine. The rate slowed to a half life of 102.6 ± 2.8 hours after about 12 hours. This sample was dosed with free chlorine to match the chloramine level. We believe more free chlorine should have been added. See text.
- i. In this experiment and initial rapid decline in chloramine was observed over the first 3 hours consistent with the rapid departure of dichloramine. After a long transition time a second slope corresponding to a half life of 83.59 ± 5.96 hours was observed. See text.
- j. In this experiment two distinct half lives were evident. See Section 5.5.4.

5.5 Traditional Means

We include under the heading “Traditional Means” allowing the water to stand, allowing the water to stand with circulation and perhaps aeration, boiling the water and the use of activated carbon filters. The other methods we consider chemical means.

5.5.1 Standing Undisturbed

In this method, the water to be treated is simply placed in a vessel and allowed to stand for a period of time without any disturbance. It is the method that we were instructed to use in the days of free chlorine only before putting our new goldfish into an aquarium filled with water from the tap. The considerations of Section 5.3 suggest that this would be the slowest means of chlorine or chloramine removal and the data of Table 4 confirm this. The water was allowed to stand undisturbed outdoors on a screened porch. The Case 1 test was done in early fall with daytime temperatures which reached into the 90's on occasion and nighttime temperatures which approached 40. The test water temperature thus fluctuated somewhat (a large mass of water changes temperature quite slowly in response to variations in air temperature. It's average temperature was probably close to 72° F. Compare the half life with the Case 10 half life. This test was carried out late enough in the fall that we thought we had better do it indoors. The indoor diurnal temperature variations were small enough that the water temperature did not vary by more than a degree or two from an average of 61° F. We feel that the difference in half lives is explained in part by the temperature difference and in part by the fact that air circulation outdoors was, at times, much greater than that indoors. Further evidence for decreased half life with increased temperature (which is entirely in accord with theory) is given in Section 5.5.4 where we show that raising water from about 60° F to boiling over an hour causes a reduction in chloramine level of about 50%.

5.5.2 Standing With Circulation

This experiment (Case 2) was the same as the Case 1 experiment and was carried out under the same environmental conditions except that the water was recirculated from a nipple at the bottom of the stockpot to the surface using a small pump. The pump ran at a rate such that 6.3 minutes were required to pump the entire 10 gallons. The water was returned at the surface but without splashing. The dramatic improvement in both free chlorine and chloramine half lives show that this method is about as effective at removing chloramine as just standing is effective at removing free chlorine.

5.5.3 Standing With Circulation and Aeration

This experiment (Case 3) was identical to the Case 2 experiment (and was carried out under the same environmental conditions) except that in addition to recirculation the water was aerated by an aquarium pump and airstone combination. Air flow is estimated at TBD LPM. We were surprised that the improvement in half life was so small. As the half lives for Cases 2 and 3 overlap when the standard errors are considered we cannot be sure whether the small improvement is real or estimation error.

5.5.4 Boiling

We have pointed out that boiling should be the most successful of any of the traditional treatments for chloramine removal because it effectively combines the benefits of circulation and aeration with increased chloramine vapor pressure due to the high temperature. The experimental data from the boiling experiments (Cases 4 and 12) confirm this but note that the half life of chloramine in our synthesized water was almost three times the half life in the Fairfax County Water Authority sample. This latter sample was most interesting in that two distinct segments with different half lives appear in the data which are shown on Figure 5.4.

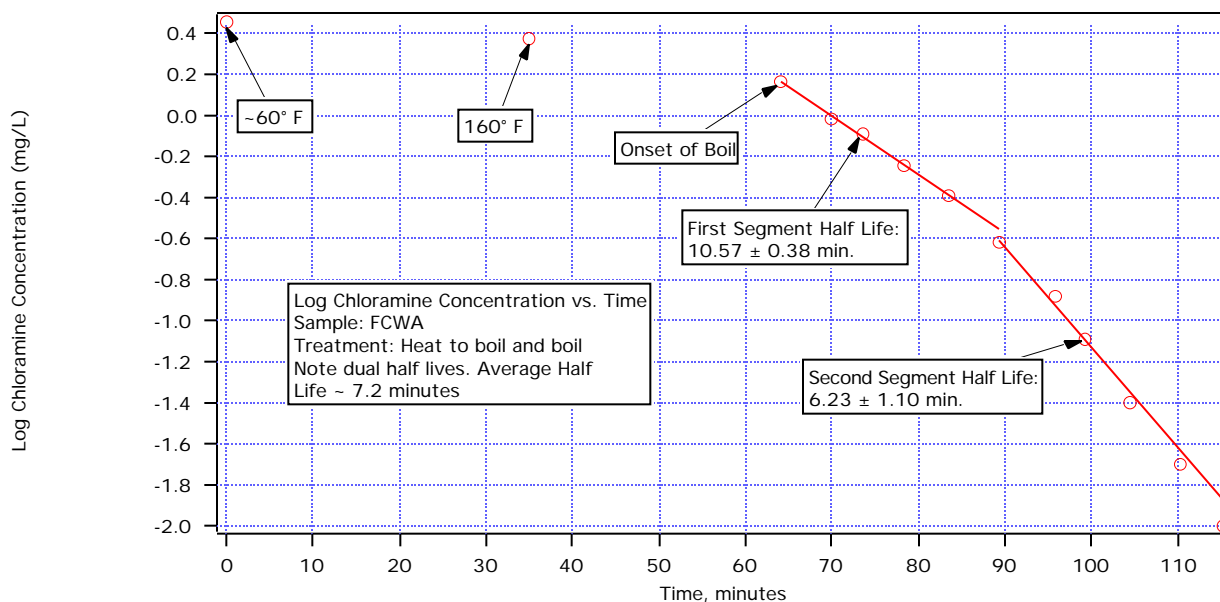


Figure 5.4 Boiling Experiment Using Ten Gallons of Water from FCWA

Figure 5.4 is interesting in other ways. First, we see that just bringing the water to a boil (which took a little over an hour with the Superb (TM) burner we used) reduced the chloramine concentration by almost exactly half. The actual concentration numbers were 2.82 mg/L at the start of heating and 1.42 at the commencement of the boil (note that a reduction to a half is represented by a log scale change of 0.301). Thus the half life for the treatment “heat to a boil” is about 65 minutes for this sample from the FCWA. Compare with the 155 minute half life for standing at 60°F. This lends support to the idea that temperature has a profound effect on half life. Second, we see that while the overall process successfully dechloraminated (and removed the very small 0.08 mg/L free chlorine as well) the water, it took nearly two hours to do this. A more potent burner would have gotten the water to boiling faster but it would still take about 50 minutes of boiling to reduce the chloramine to the terminal 0.01 mg/L of this experiment. During an hour’s boil one can expect 10 - 20% of the original water volume to be lost. Comparing the Case 12 results with Case 4 we conclude that boiling will remove chlorine and chloramine completely but that it may not be a practical approach unless

- The water is to be boiled anyway for decarbonation
- The brewer does not wish to use a chemical method

5.5.5 Active Carbon Filtration

Active carbon filtration is a good candidate for removing chlorine and chloramine and is the method of choice for commercial breweries. Even waters which are not chlorinated or chloraminated benefit from this treatment because exposure to activated carbon removes not only chlorine and nitrogen compounds but many other organics as well, especially those which may contribute color or odor to the water. Though organics are removed by activated carbon treatment, inorganics are not and so desirable minerals in the water are not removed. We mention this because a home brewer is likely to implement activated carbon filtration with a counter top unit such as the Brita(TM) which contains not only the activated carbon but also ion exchange resins which will remove calcium, magnesium, sulfate etc. from the water as well as chlorine/chloramine. There are other activated carbon options available to the home brewer but these involve plumbing (and its expense) and maintenance.

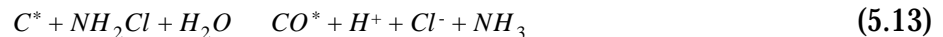
Small, under the counter units with replaceable cartridges are available as well as larger “whole house” units. These may be in the form of the typical cartridge filter commonly used in swimming pool installations and more familiar to brewers in the forms which we use to filter yeast from our beer. The cartridge is replaced when chlorine is detected in the output water either by smell or by a test such as the ones described in Section 6.0. Other whole house units are in the form factor of the typical water softener or neutralizer. The medium in this filter must be replaced in the same manner as the media in the softener or neutralizer. Media can be rejuvenated but this is not practical for the brewer to do himself as roasting at high temperature is required.

Chlorine and chloramine oxidize activated carbon sites (Ref 14.) and are, in the process, reduced to chloride ion and, in the case of chloramine, ammonia or ammonium ion. For chlorine the reaction is

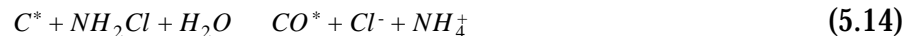


where, in the notation of Ref 14., C^* represents an activated carbon site and CO^* a surface oxide. This reaction shows that each mole of chlorine reduced by the carbon is converted to a mole of chloride ion. As a mole of chloride ion and a mole of chlorine weigh almost exactly the same, it is clear that each mg/L of chlorine will be converted to 1 mg/L of chloride. The reaction also releases 1 mole of hydrogen ions for each mole of chlorine processed. In order that chlorine and chloramine tests can be compared, test chemistries are calibrated such that it is the amount of chlorine which is indicated, not the amount of hypochlorite or chloramine. Thus if a test reads 1 mg/L this means that the chlorine bearing substance, whatever it is, is present in an amount which contains 1 mg/L chlorine. As the atomic weight of chlorine is 35.45, each mg/L chlorine is equivalent to 1/35.45 or 0.0282 millimole/L. The reaction thus indicates that each mg/L chlorine treated will release 0.0282 millimoles of hydrogen ions. As hydrogen ions have a charge of 1, this amount can also be described as 0.0282 milliequivalents per liter. These hydrogen ions will “neutralize” 0.0282 milliequivalents per liter of alkalinity. Alkalinity is usually expressed in mg/L or ppm as $CaCO_3$. The value in these units is found by multiplying the milliequivalents per liter by 50. Thus for each mg/L chlorine in the water, a reduction in alkalinity of 1.41 ppm as $CaCO_3$ is effected when the water is run through an activated carbon bed.

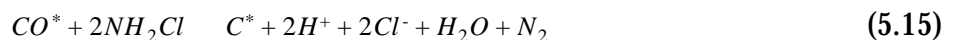
For monochloramine the reaction is



At lower pH we'd expect to see ammonium ion formed:



Once some surface oxide is formed, however, the chloramine is oxidized by it:



thus regenerating the activated carbon site. The net reaction at the lower pHs associated with brewing, obtained by

combining these last two equations, describes the steady state flow situation:



in which we see that two thirds of the chloramine destroyed is oxidized to nitrogen while one third is reduced to ammonium ion. Each mg/L of chlorine is reduced to 1 mg/L chloride as before but only two thirds the hydrogen ion is produced (i.e. it takes 3 chlorines to produce 2 hydrogens whereas with free chlorine 3 chlorines would produce 3 hydrogen ions). Thus in the steady state there is a 0.94 ppm reduction in alkalinity for each mg/L chlorine. Each millimole of chlorine produces one third of a millimole of ammonia. Thus each mg/L chlorine yields 0.0094 millimole/L or approximately 0.17 mg/L. The ammonia is of no concern to us as brewers as we have already noted. It is of theoretical interest here to note that were all the chlorine monochloramine, the activated carbon would never need replenishment. This ideal condition would never be met in real life and so indeed the carbon must be renewed periodically.

As water percolates through a carbon bed chlorine and chloramine are removed gradually over the contact time. Thus chloramine and chlorine have half lives within the filter. In researching this article we tested a sample of the Brita (TM) pitcher type of filter. It would be, of course, difficult or impossible to measure what is going on inside the cartridge. Therefore we measured chloramine levels at the input and output of the cartridge. We found that the filter cartridge in the test unit removed about 84% (i.e. 16% remains) of the chloramine in the test sample. Thus water at 1.51 mg/L chloramine poured into unit in our test unit measured 0.25 mg/L in the pitcher. Poured through the filter again the water measured 0.04 mg/L in the pitcher. Thus we conclude that units of this type are effective at removing chloramine though more than one pass may be required⁶. The manufacturer's specification sheet included with the unit claims a reduction of free available chlorine from 2 mg/L to 0.15 mg/L i.e. a reduction of 92.5% (7.5% remains). We did not verify that number but have no reason to disbelieve it.

As we mentioned earlier, the Brita, and similar units, contain ion exchange resins in addition to the activated carbon elements. The purpose of these is to remove cations, in particular lead and copper but other cations, and anions, are removed as well. This was verified by qualitative tests - water passed through the test unit was virtually devoid of hardness (magnesium, calcium) and alkalinity (bicarbonate). Water treated by one of these devices for chlorine/chloramine reduction will require at least supplemental calcium and sulfate for most brewing applications and should be thought of as deionized water.

5.6 Neutralizing Residual Chloramine Chemically

Previous Sections have shown that standing (even with circulation and aeration) will require a long time to reduce chloramine (and even chlorine) to desirably low levels. Boiling is more effective in terms of time required but boiling is a nuisance and requires energy so that it isn't a very attractive option unless it is going to be done anyway. In this section we discuss chemical means for removing chloramine from brewing water. Of the three we find the first described, the Campden tablet method, the most appealing as only a very small quantity of a readily available food grade product commonly used in wine and mead making is required. It is the only "pure" chemical method in that it converts chloramine and chlorine to other harmless substances which remain in the water. The other two methods try to convert monochloramine to more volatile dichloramine which would then leave the water faster than monochloramine under one of the traditional treatment methods.

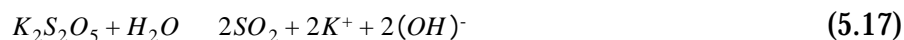
⁶ The concentration remaining after n passes is $C = C_0 \frac{r}{100}^n$ where C_0 is the original concentration and r is the percentage remaining after 1 pass.

Neither of these latter two methods is ready to be recommended to the brewing community. They are described here in the hopes that readers will find them interesting and that others will be encouraged to experiment. The first of these two methods might be practically applicable in a pinch but it is not fully understood (at least by your author) at this point. It requires the addition of household bleach to the water. While household bleach is commonly used to sanitize wells and is the recommended disinfectant for water in times when the municipal supply is not safe or is interrupted, household bleach is not a food product and we do not feel comfortable recommending that it be put into brewing water. The other requires that the water be acidified with a strong mineral acid and then neutralized with a strong mineral base. We don't recommend that homebrewers handle such chemicals but this method might be of some interest to commercial brewers.

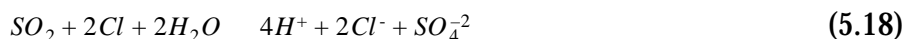
5.6.1 Campden Tablets

We indicated in the introductory material that aquarists reduce chloramine by means of a reducing⁷ agent and we propose that a brewer can easily do the same thing to get rid of chloramine (and chlorine). Whereas the aquarist prefers sodium thiosulfate, the brewer, especially if he also makes mead or wine, is likely to have potassium metabisulfite (more properly called potassium pyrosulfite) in the form of Campden⁸ tablets or sodium metabisulfite (more properly called sodium pyrosulfite) in the form of powder in his cupboard. Not only is metabisulfite a fine reducing agent but its by-products are sulfate and ammonium ions. Both are beneficial to beer in reasonable quantities and, as we shall see, the quantities of these ions released in neutralizing a few mg/L of chloramine or chlorine are insignificant.

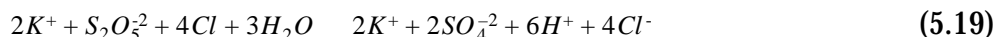
Metabisulfite is often thought of by vintners as sulfur dioxide in solid form and indeed Campden tablet bottle labels often contain a notation such as "55% sulfur dioxide". The reaction



shows how this basic salt reacts with water to produce SO_2 . In the normal wine making use of Campden tablets (or powdered sodium metabisulfite, it is the SO_2 residual in the wine which is sought because of its ability to suppress the growth of wild yeast. In the present application SO_2 reduces chlorine:



The "sum" of twice the second equation with the first gives the overall reaction:



thus each millimole of available chlorine atoms consumes one quarter of a millimole of bisulfite, produces half a millimole of sulfate and potassium ions, 1 millimole of chloride ions and 1.5 millimoles of hydrogen ions. Consider a water sample containing 3 mg/L chlorine. The atomic weight of chlorine is 35.45 so this is 0.0846 millimoles per liter mM/L. One quarter of this (0.0211 mM) of metabisulfite is required. Potassium metabisulfite (Campden tablets) has a

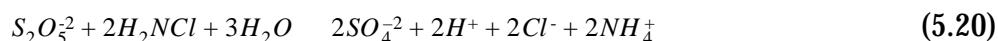
⁷. "Reducing" does not mean that the agent reduces quantity of chloramine or chlorine, though it does. "Reduction", in this context, is the chemical opposite to oxidation. Whereas oxidation refers to the taking of electrons, reduction means the donation of electrons.

⁸. We believe that Campden tablets sold in Britain are sodium metabisulfite and have been told by correspondents that Campden tablets they have bought in the US are also sodium metabisulfite. The Campden tablets we worked with (Crosby and Baker) are potassium metabisulfite.

molecular weight of 222.32 mg/mM so that 4.7 mg/L of that salt would be required. We note that a Campden tablet weighs about 695 mg of, presumably, nearly pure potassium metabisulfite and should, by these calculations, be capable of clearing 147 liters or 39 US gallons of water. Sodium metabisulfite is usually supplied as a powder. Its molecular weight is 190.1 so that 4.0 mg/L of that salt would be required to eliminate the 3 mg/L of chlorine.

As Equation (5.19) shows each chlorine atom gets converted to a chloride ion which weighs the same as the atom (ignoring the mass of the added electron) and so the 3 mg/L chlorine converted to 3 mg/L chloride ion. In addition, 0.0423 mM/L of sulfate or about 4 mg/L and 0.126 mM of hydrogen ions (which cancel 50 times this or 6.34 ppm as calcium carbonate alkalinity) are generated.

Where chloramine is involved the reduction is given by



thus each millimole of available chlorine requires half a millimole of bisulfite and produces 1 millimole of sulfate, 1 of chloride, 1 of ammonium ions, 1 of potassium and 1 of hydrogen ions. Using the same example of 3 mg/L chlorine but in the form of chloramine this time we'd need 9.4 mg/L of potassium metabisulfite (thus one tablet would treat about 20 gallons of water) or 8 mg/L sodium metabisulfite and have 3 mg/L chloride, 8 mg/L sulfate, 1.5 mg/L ammonium ions at the completion of the reaction. Alkalinity would be reduced about 4.2 ppm as calcium carbonate.

Our recommendation of 1 Campden tablet per 20 gallons is designed to cover this nominally "worst case" of 3 mg/L chlorine all as chloramine. In most cases this will be more than required and there will be sulfur dioxide left over after the chlorine has been reduced. Some of this will be driven off when the wort is boiled but some of it will react with organics in the mash reducing them. This results in the formation of "reductones", i.e. reduced state substances which are considered desirable as they are supposed to prevent oxidation and staling. In reducing organic material in the mash, the sulfur dioxide is converted to sulfate. If all of it undergoes this fate then the maximum found in a brew made from water treated with one Campden tablet per 20 gallons will be about 8 mg/L as calculated above.

More precise dosing of metabite can be determined by measuring the levels of free and available chlorine. A another convenient rule of thumb is a refinement to the 1 tablet per 20 gallon rule. Add twice the chloramine value to the free chlorine value and divide by 6. This is the number of tablets required for 20 gallons. Scale this value according to how many gallons need to be treated. To add fractional tablets, dissolve, or rather suspend, a tablet in 100 mL of water and, just after agitating, measure out the number of mL which corresponds to the percentage fraction required. For example, if a third of a tablet is required, measure out 33 mL.

Even more precise calculations can be done from the free and chloramine measurements using the data of Table 5. Decide whether Campden tablets or sodium bisulfite are to be used. Find the mg/L of the chosen salt required for free chlorine and multiply by the mg/L free chlorine. Now multiply by the number of liters of water to be treated. This is the salt requirement for free chlorine. Now do the same for monochloramine to calculate the salt requirement for monochloramine. Sum the two salt requirements (and divide by 695 to obtain the number of Campden Tablets if this is the form of metabite to be used). Consult the entries in the table for amounts of ions which will be added as a consequence of the treatment.

Example: 200 liters of water with free chlorine at 1.5 mg/L and monochloramine at 2 mg/L are to be treated with Campden tablets. The requirement for the free chlorine is 2.346 mg/L times 200 liters or 469.2 mg. The requirement for monochloramine is 6.254 mg/L times 200 litres or 1250.8 mg. The total is 1720.0 mg which is about 2 and a half Campden Tablets. Potassium in the amount of about 3 mg per liter will be added by this treatment. Sulfate will go up by 7.4 mg/L, 1 mg/L ammonium ion will be added, chloride will increase by 3.5 mg/L and alkalinity will decrease by 6 ppm as CaCO₃.

As with any chlorine/chloramine treatment it is advisable to run a post treatment check when using metabite. Our experiments have shown that perhaps 20 to 30% more metabite than calculated should be used to be on the safe side. This represents a modest increase in the amount of by-products. Also be aware that not all Campden tablets weigh 695 mg nor are they all, apparently, potassium metabisulfite. The weight of the Campden tablets should be obtained (weigh lots of them on a kitchen scale or reloading scale and divide by the number if a lab balance is not available). If uncertain as to whether they are the potassium or sodium salt have the supplier check with his supplier or assume they are potassium. If you guess wrong, you will be adding 17% more bisulfite than you need. This is not a significant amount.

Table 5: Treatment 8: Bisulfite Required and Ions Liberated

	Per mg Free Chlorine	Per mg Monochloramine
mg Potassium Metabisulfite Only ^a (Campden Tablets ^b) Required	1.564	3.127
mg Potassium Added (Campden Tablets Only ^c)	0.550	1.100
mg Sodium Metabisulfite Only ^d Required	1.337	2.674
mg Sodium Added (Sodium Metabite Only ^e)	0.323	0.646
mg Sulfate added	1.35	2.70
mg Ammonia added	0	0.51
mg Chloride added	1.0	1.0
Alkalinity neutralized (mg/L as CaCO ₃)	2.11	1.43

a. The values given are those required to neutralize the chlorine and chloramine when only potassium metabisulfite is used.

b. A Campden Tablet weighs about 695 mg

c. Potassium is only added when potassium metabisulfite is used.

d. The values given are those required to neutralize the chlorine and chlorine when only sodium metabisulfite is used.

e. Sodium is added only when sodium metabisulfite is used.

5.6.2 Bleach

We noted earlier by Equation (4.2) that hypochlorite is capable of oxidizing monochloramine to dichloramine and so reason that where most of a sample's chlorine is in the form of monochloramine we might be able to speed it on its way by converting it to dichloramine and achieve this by the addition of hypochlorite in the form of bleach. Any excess chlorine (i.e. chlorine which does not oxidize monochloramine) should escape the water at free chlorine rates.

We did two experiments (Cases 6 and 11) in which this technique was tried. In the Case 6 experiment we dosed our synthesized water with bleach to the point where the free chlorine level was 1 mg/L higher than the chloramine level and then allowed the water to stand. Figure 5.5 shows what happened. After addition of free chlorine, in the form of household bleach⁹. The chloramine concentration rose and then dropped precipitously exactly in accordance with our expectations.

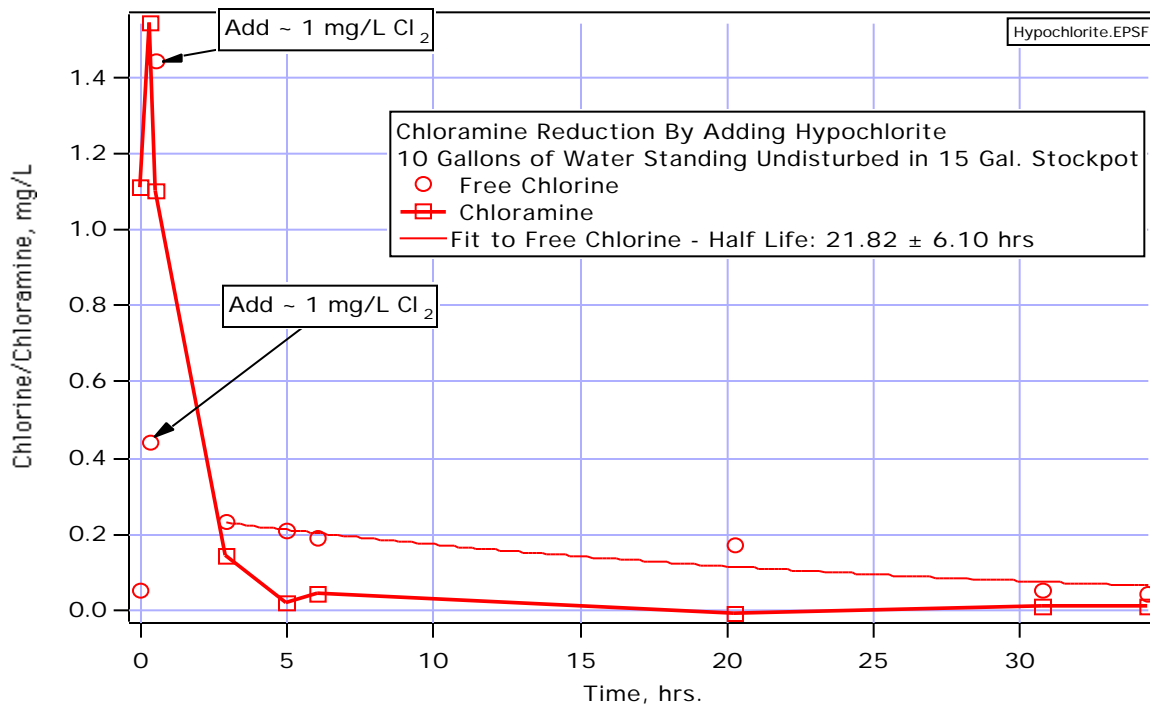


Figure 5.5 Chloramine Reduction by Oxidation of Monochloramine to Dichloramine Using Bleach

⁹. Bleach is sold as a solution of sodium hypochlorite. Household bleach is about 5 “trade percent”. This is the effective concentration of chlorine on a weight per volume basis. Thus 5 trade percent bleach contains 50 grams of chlorine per liter or 50 mg/mL. To add 1 mg/L chlorine to 10 gallons of water (38 L) thus would require the addition of approximately 0.8 mL of 5% bleach.

In the Case 11 experiment, free chlorine (again in the form of household bleach) was added to a sample of FCWA water but this time just to the extent of the chloramine concentration. Again, the chloramine level rose dramatically and then fell quickly (half life 16.8 hours) but not even as far as the original level. Free chlorine did quickly drop to the original level confirming that the added chlorine did convert to chloramine. Chloramine continued to leave the water but at a much slower rate (half life 102.6 hours) which is faster than the rate at which chloramine leaves this water without treatment but not so fast that we could recommend this procedure to the reader, at least not yet. We think the answer is a higher initial dose of free chlorine but need to experiment further.

In neither Case 6 nor Case 11 did we adjust the pH of the sample. As we see in the next Section, pH reduction enhances chloramine removal.

5.6.3 Acidification

At low pH monochloramine converts to dichloramine which, as we saw above, clears quickly from even standing water. Thus we suggest that chloramine can be disposed of by reducing the pH of the water to be treated to near pH 4, allowing the dichloramine to escape, and then restoring the pH to a higher value suitable for dough in. The amount of acid required is easily calculated as being approximately equal to the alkalinity of the water when that parameter is expressed in mEq/L. To convert the more commonly seen ppm as CaCO₃ to mEq/L simply divide by 50. For example, water with alkalinity of 100 ppm as CaCO₃ has alkalinity of 2 mEq/L and would require 2 mEq/L of acid to treat it. To treat 10 gallons (38 L) of such water would require 76 mEq of acid which would be about 13 mL of 50% hydrochloric acid solution (a common strength) which is about 6 N (contains about 6 mEq/L). Clearly, we have added 2 mEq/L of the acid cation (70 mg/L chloride ion in the case of the current example) and this must be considered.

To neutralize the acid after the chloramine has been removed would require the same amount of base or basic salt. In the example we have been using here this is 2 mEq/L. Obvious choices of bases are calcium hydroxide and sodium hydroxide though calcium carbonate, sodium carbonate, potassium hydroxide etc. could also be used. We favor calcium hydroxide as it can be purchased as food grade "pickling lime" in most supermarkets. The 2 mEq/L required would add 40 mg/L calcium to the water and another reason for favoring calcium hydroxide is that it would be hard to imagine a situation where an extra 40 mg/L of calcium would be a detriment to a brew. Because of this mEq for mEq mineral anion (chloride, sulfate, phosphate) and cation (calcium, sodium, potassium) addition for each mEq of alkalinity, it is clear that this method has more appeal for waters with low alkalinity.

In our single experiment (Case 7) with this technique hydrochloric acid was added to our synthetic water. Chloramine levels did subsequently drop under undisturbed standing conditions with a half life of 20.9 hours, a little faster than that for free chlorine under the same circumstances. We will be experimenting further with this technique as well.

6.0 Testing for Chlorine

Chlorine is such a simple thing to test for that there is no reason why any brewer concerned about the levels of chlorine in his water and the effectiveness of his remediation method should not be checking levels of both free and bound chlorine. Test kits are available in many levels of sophistication (and cost) from several sources. The simplest and quickest place to get a test kit is the local pet store. Interestingly enough these kits, sold for use by the public, contain poisonous orthotolodine used to measure free chlorine and the even more so Nessler's reagent to estimate the ammonia released by chloramine. If you obtain such a kit, treat the chemicals in it with respect.

Analysis laboratories have gravitated away from orthotolodine in favor of DPD (N,N-diethyl-p-phenylenediamine) in part because of the toxicity but also because of accuracy. Most kits obtained from a lab supply source will be based on DPD. DPD is colorless in its reduced state but when oxidized it turns magenta forming what is known as Würster Dye. When added to a sample containing free chlorine (or another oxidizing agent) the depth of magenta color formed depends on the amount of the oxidizer present. When combined chlorine is to be measured potassium iodide is added to the sample with the DPD. The chlorine in chloramine has the ability to oxidize the iodide ion to free iodine and the iodine then in turn oxidizes the DPD causing the conversion to Würster Dye. Thus to get a complete picture of the status of a water sample with respect to chlorine using DPD we run two tests: the first, employing iodide and DPD gives an indication of the total chlorine (free plus chloramine bound). The second uses DPD alone and measures the free chlorine only. The estimated chloramine level is taken as the total chlorine test result minus the free chlorine test result.

The depth of the color developed when DPD is oxidized can be judged in several ways depending on the sophistication of the test and accuracy required. Note that great accuracy is not required of a brewer unless he wants to take several measurements for the purpose of estimating half life. More typically the brewer is looking for a 0 reading i.e. an indication that he has successfully rendered his water chlorine/chloramine free. In simple, inexpensive kits the water and DPD (plus iodide if a total test is being done) with suitable pH buffers are placed in a small test tube and allowed to react. The color of the test tube is then compared to colored patches printed in the instructions or on the side of the carton in which the kit was shipped. In other inexpensive implementations the test tube is integral with a fixture which contains built-in color comparison patches. In either case the value is read from the patch which most closely matches the color of the liquid in the tube. More expensive kits will contain a transparent wheel around whose edge a colored strip of variable density Würster dye has been printed. A small portion of this wheel is viewed through an aperture adjacent to the tube containing the test water plus DPD. The wheel is rotated until the best color match is obtained and the chlorine amount read from a scale on the periphery of the wheel. In some cases, the light passing through the wheel passes first through a second tube containing the test water to which no chemical has been added. This removes the effects of any color in the water itself.

If more accurate results are desired the depth of color can be measured by a spectrophotometer or colorimeter configured to measure light absorbance at 530nm. The chlorine concentration (free or total) is read from a calibration curve determined by the analyst using chlorine solutions of standard strength, supplied by the manufacturer or programmed into the instrument. The most sensitive and accurate measurements are made using a technique called "amperometric titration" in which the current flowing between a pair of biased inert electrodes is monitored as a reducing agent is gradually added to a test sample. The equipment is expensive and requires a skilled operator. Brewers would be unlikely to encounter this method of measurement.

Full details of these and other methods of chlorine measurement can be found in Ref. 15. Most of the available kit chemistries are based on the procedures set forth in this reference.

7.0 Summary

We would like to finish up with a summary of what the author feels are the significant findings of the investigation to date:

- Brewers are more likely to encounter chloramine than they have been in the past
- Chloramine is more difficult to remove from water than free chlorine
- Chloramine can be removed by boiling though an extended boil may be required

- Chloramine can be effectively removed by means of an activated carbon filter
- Chloramine can be effectively removed by addition of Campden tablets
- Chloramine can be removed by allowing the water to stand but recirculation is required and temperature should be elevated. Even so, reduction to an acceptable level may take several days.
- The effectiveness of any chloramine reduction attempt should be checked using a simple, inexpensive test kit which is sensitive to chloramine as well as chlorine

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