

Evaluation of Dechlorinating Agents and Disposable Containers for Odor Testing of Drinking Water

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(Abstract)

As the bottled water trend continues to rise across the nation, drinking water utilities have become more concerned with ensuring consumer satisfaction of their product. Although public water supplies are safeguarded by regulations, aesthetically unappealing taste-and-odor problems have led consumers to search for alternative water sources, such as bottled water or tap water processed by point-of-use filters. Consequently, taste-and-odor monitoring has become important to the drinking water industry. Because many utilities use chlorine to disinfect the water, chlorine odor often masks other more subtle odors that may eventually cause consumer complaints. As treated water travels from the water treatment plant to the consumer, chlorine residual diminishes and may reveal a water's naturally less-pleasing odors. Consequently, odor monitoring at the water treatment plant, where chlorine concentrations are at a peak, may not identify potential displeasing smells. Proper evaluation of these odor-causing substances requires that the chlorine odor first be eliminated before evaluating any remaining odors. Dechlorinating agents can remove chlorine, but some will produce other unwanted odors or even remove certain odorous compounds. This research describes the efficiency of several of these agents (ascorbic acid, hydrogen peroxide, oxalic acid, sodium nitrite, and sodium thiosulfate) in dechlorinating chlorinated solutions of the earthy-smelling compound geosmin and musty-smelling MIB.

Interfering odors in reusable containers pose another problem in drinking water odor analysis. The most common odor-analysis methods (TON and FPA) involve the use of glass flasks, which often either develop chalky odors or have persistent lingering odors from previous evaluations. Furthermore the glass flasks break easily and are difficult to clean. This research also evaluates the suitability of four types of disposable plastic containers for odor analyses.

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Author's Preface

Each chapter of this thesis is a separate manuscript and has been prepared according to the format guidelines of the particular journal to which it shall be submitted. The first chapter entitled "Introduction and Project Background" is a comprehensive review of the literature and research "Interactions Among Various Dechlorinating Agents and Taste-and-Odor Causing Compounds" will be submitted to the *Journal of the American Water Works Association*. The final chapter entitled "Investigation of the Sensory Attributes of Alternative Containers for Use in Drinking Water Odor Analysis" will also be submitted to the *Journal of the American Water Works Association*.

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Part I: Project Background and Literature Review

Introduction

Although public water supplies are safeguarded by governmental standards, unregulated, aesthetically unappealing taste-and-odor problems can be readily apparent to consumers. Especially common are the compounds geosmin and 2-methylisoborneol (MIB), which, respectively, cause earthy and musty tastes and odors at the nanogram per liter level. While these problematic odor compounds are often treatable with activated carbon, the process can be expensive and difficult to implement. Furthermore, some taste-and-odor events may be periodic or even seasonal in nature, but often others are unpredictable in both time of occurrence as well as location in the water system. Consequently, taste-and-odor monitoring, to detect and avoid odor problems before they cause consumer complaints, has become important to the drinking water industry.

Sensory evaluation is the most common method of taste-and-odor monitoring. While larger, better-equipped water utilities may use analytical techniques such as gas chromatography, most smaller utilities can not support this technique. Furthermore, time-consuming sample-concentration methods, such as solid-phase microextraction (SPME) or closed-loop stripping analysis (CLSA), are required for accurately measuring the low levels of contaminants. Sensory evaluation can identify taste-and-odor-causing compounds at levels below those that can be detected by a gas chromatograph. Furthermore, sensory testing is usually less expensive and less time-consuming than analytical techniques that require expensive instrumentation.

Unfortunately, one problem often encountered in sensory evaluation is the masking effect of chlorine on odor-causing compounds. Because many utilities use chlorine to disinfect the water, chlorinous odors often mask other more-subtle odors that may eventually cause consumer complaints. As finished water travels from the water treatment plant to the consumer, the chlorine residual can diminish and unmask these less-pleasing odors. Consequently, odor monitoring at the treatment plant, where chlorine concentrations are usually at a peak, may not identify potential displeasing odors. Before these odor-causing substances can be properly evaluated, it is desirable to first remove the chlorine odor and then evaluate any remaining odors. Dechlorinating agents can remove chlorine odors, but some may either produce other unwanted odors or even remove the odorous compounds themselves. An ideal dechlorinating agent is one that will: (1) effectively remove chlorine but not the odor-causing compounds, (2) have no perceivable odor of its own, (3) not produce new odors, and (4) reveal underlying odor compounds present in the water sample.

Another problem often encountered during odor evaluations is the interference of odors arising from water containers. Over the years, many different types of containers have been used during drinking water odor analyses, including plastic and glass containers of various shapes and sizes. Today, a popular method of taste-and-odor evaluation is flavor profile analysis (FPA) in which 500-mL wide-mouth glass Erlenmeyer flasks are used. The benefits of using this flask are that it can be stoppered while being heated in a water bath and it is easy for panelists to swirl samples immediately prior to sniffing, releasing compounds into the large headspace. Unfortunately, cleaning the flasks to effectively rid them of lingering odors is a time-consuming process. Furthermore, the glass often develops a chalky odor when the flasks are washed and dried.

Often, drinking water odor evaluations are performed many times over the course of a day. Furthermore, the on-duty utility operator is occasionally the only one involved in these evaluations and may not have the time to effectively clean the flasks, resulting in unwanted interference during sensory evaluations.

While plastic polymer containers have been used in the past for odor analyses, several odor interferences have been noted. The origin of these interferences has not been well defined, and only limited information on the odor characteristics of specific polymers is available. The research described in this paper examined the odor characteristics of several disposable plastic containers and compared their odor properties to those of glass Erlenmeyer flasks. The objectives of this project were to:

- Assemble an odor panel and train the individuals according to flavor profile analysis (FPA) protocol described in *Standard Methods for the Examination of Water and Wastewater* (APHA et al. 1995).
- Generate Weber-Fechner plots for chlorine and geosmin as a means of comparing the panel's sensitivity and reliability to previous research.
- Review the scientific literature and identify suitable dechlorinating agents for taste-and-odor analysis.
- Test dechlorinating agents for their efficiency at removing chlorine in aqueous solutions.
- Choose several of the more effective dechlorinating agents for sensory testing and identify one or more that would remove chlorine without altering residual odor compounds.
- Evaluate, by sensory analysis, the odor characteristics of water in several types of disposable plastic containers and determine their suitability for use in drinking water odor analyses.

Literature Review

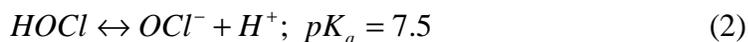
Chlorine

History. For centuries civilization has practiced various methods of drinking water disinfection. The first documented treatment occurred around 2000 BC, when two Egyptian medics prescribed a system of exposing foul water to sunlight, treating it with hot copper, and filtering it through charcoal (Baker 1981). Other early disinfection methods included heat and storage, ultraviolet irradiation, application of metals such as silver and copper, pH adjustment, and oxidant treatment (Connell 1996). Chlorine was first synthesized in 1774 when Karl W. Scheel heated hydrochloric acid with manganese oxide (Bryant et al. 1992). Early chlorine disinfection of drinking water began in England (Connell 1996), gaining popularity in the late 1800's as a means of controlling the spread of waterborne diseases such as typhoid, cholera, and dysentery. The first American patent for chlorine disinfection was granted in 1888 to Albert Leeds (Faust 1999). Afterwards, chlorine disinfection quickly spread across the United States, with the first continuous chlorine application occurring in 1908 at the Boonton, New Jersey drinking water facility (Baker 1981).

As the popularity of chlorine disinfection grew, so did its dosage in drinking water treatment. Gradually scientists became aware of the harmful side reactions resulting from chlorination. In the 1970's, Rook (1974) and Bellar et al. (1974) independently identified reactions between chlorine and dissolved organic matter that produced compounds known as trihalomethanes (THMs), which are suspected cancer-causing byproducts of the disinfection process. In 1974, the United States Congress passed the Safe Drinking Water Act (SDWA), which established the basis for more stringent drinking water standards, including regulation of the concentration of

THMs. In 1979, the United States Environmental Agency (USEPA) promulgated a THM maximum contaminant level (MCL) of 0.10 mg/L (*Federal Register* 1979). Since the discovery of THMs, chlorine use has come under scrutiny, resulting in the increased use of more expensive and complicated disinfection methods, including chloramination, ozonation, ultraviolet irradiation, and chlorine dioxide addition. Ongoing and future research aims to better understand chlorination chemistry and disinfection byproduct (DBP) formation, which will result in improved disinfection methods.

Chemistry. Chlorine has several oxidation states, giving rise to various chemical forms, including molecular chlorine (Cl_2), hypochlorites (frequently NaOCl or $\text{Ca}(\text{OCl})_2$), and chloramines (predominantly NH_2Cl , NHCl_2 , or NCl_3). As molecular chlorine is introduced into water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) are formed according to the following equations:



Collectively, Cl_2 , HOCl , and OCl^- are referred to as the “free chlorine” species. As equation 2 illustrates, HOCl and OCl^- are in equilibrium, with their respective concentrations being dependent upon pH, temperature, and dissolved solids (Palin 1975). This equilibrium is vital to effective chlorination as hypochlorous acid (HOCl) is the more effective disinfectant. Figure 1.1 shows the distribution of the various free chlorine species over a wide range of pH values. As depicted, hypochlorous acid dominates as the most abundant species over the majority of pH values but is in equilibrium with hypochlorite ion at pH 7.5.

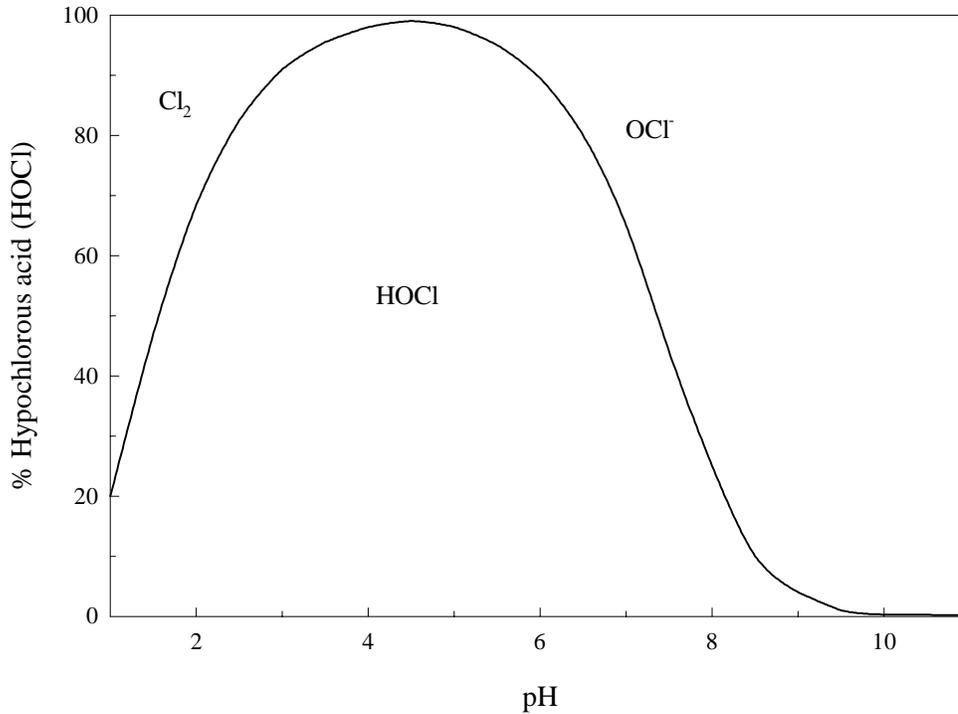
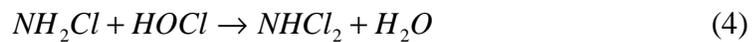
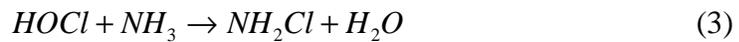


FIGURE 1.1 Distribution of chlorine species with varying pH (adapted from Bryant et al. 1992).

Chloramines are produced when available nitrogen reacts with free chlorine species. The most common chloramines (monochloramine, dichloramine, and nitrogen trichloride) are produced from ammonia and free chlorine according to the following equations (White 1999):



The chloramine species are known collectively as the “combined chlorine” species and are produced more slowly than the free chlorine species. Chloramine concentrations fluctuate

depending on pH, temperature, chlorine to ammonia ratios, and contact time (White 1999). For example, lower pH values and higher chlorine-to-ammonia ratios generally produce the more highly chlorinated species (nitrogen trichloride) (Palin 1975). In the pH range of most drinking waters (7.0-8.0), monochloramine dominates as the most abundant combined chlorine species (Palin 1975).

Together, free and combined chlorine species provide the disinfecting power of chlorination. The instantaneous reaction time of HOCl makes it the more effective chlorine species, approximately 80 times more powerful than OCl^- (Palin 1975). Factors such as contact time and ease of chemical use may affect a water utility's choice of disinfectant. When contact time is not a limiting factor, chloramination may prove more advantageous to some utilities, but it cannot be used as the "primary" disinfectant. Most often utilities use one of the many free chlorine substances, including molecular chlorine gas and hypochlorite salts. Most large-scale water treatment facilities use molecular chlorine gas, pressurized to a liquid, to disinfect their water. Smaller utilities tend to use the solid hypochlorite salts, such as calcium or sodium hypochlorite, as they are easier to handle, less likely to release hazardous chlorine gas, and can be easily fed by simple pump systems. Used properly, all of the chlorine species effectively inactivate pathogenic bacteria, viruses, and protozoa.

Aroma and Flavor. With the increased chlorination of drinking water in the 20th century came consumer discontent with resultant chlorinous tastes and odors. While these unpleasant effects of the chlorination process do not pose any known health risks, consumers desire a water that is both safe and pleasing to drink. Bryan et al. (1973) evaluated chlorine taste thresholds at various

pH values, finding a threshold of 0.075 mg/L (as Cl₂) at pH 5.0; 0.156 mg/L at pH 7.0; and 0.450 mg/L at pH 9.0. Later, Krasner and Barrett (1984) evaluated both the taste and odor thresholds of individual chlorine species, finding the values shown in Table 1.1:

TABLE 1.1
Chlorine Odor and Taste Thresholds

Compound	pH	Odor Threshold (mg/L as Cl ₂)	Taste Threshold (mg/L as Cl ₂)
Hypochlorous acid	5.0	0.28	0.24
Hypochlorite ion	10.0	0.36	0.30
Monochloramine	8-9	0.65	0.48
Dichloramine	4.0	0.15	0.13

(adapted from Krasner and Barrett 1984)

Chlorine concentrations in typical drinking water supplies range from 0.5 to 2 mg/L as Cl₂, which are sufficiently high to produce strong chlorinous odors. Concentrations at the treatment plant, where odor monitoring usually occurs, can be as high as 4 mg/L as Cl₂. At these levels, chlorine can severely interfere with sensory odor evaluations.

Taste-and-Odor Compounds

Most taste-and-odor complaints in the drinking water field are caused by chlorine, geosmin, and 2-methylisoborneol (MIB) (Suffet et al. 1996). While chlorine is applied to water for disinfection purposes, geosmin and MIB are algal metabolites that contaminate source waters during periods of cyanobacterial bloom (blue-green algae). Filamentous bacteria known as actinomycetes, also produce geosmin and MIB and are commonly found in drinking water supplies. In fact, geosmin was first isolated in 1965 from actinomycetes and was named to reflect its characteristic odor (*geo*, Gr. “earth” and *osme*, Gr. “smell”) (Gerber and Lechevalier 1965). Its structure was not described, however, until 1968 (Gerber 1968; Medsker et al. 1968). Since then, geosmin has been isolated from many species of actinomycetes and blue-green algae.

Its odor threshold is in the range of 5-10ng/L (Mallevalle and Suffet 1987; Rashash et al. 1997). In 1969, musty-smelling MIB was also isolated from actinomycetes (Gerber 1969; Medsker et al. 1969). Its odor threshold is approximately 10ng/L (Mallevalle and Suffet 1987; Krasner et al. 1983). Figure 1.2 depicts the structures of these compounds:

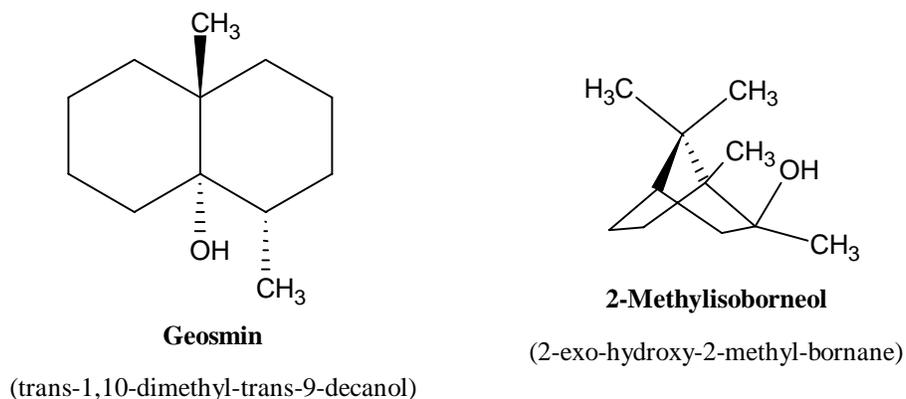


FIGURE 1.2 Chemical structures of geosmin and 2-methylisoborneol

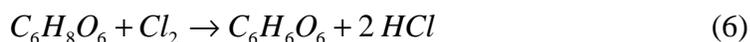
Although both geosmin and MIB can be effectively removed during drinking water treatment with activated carbon (Lalezary et al. 1986; Lalezary-Craig et al. 1988; Suffet et al. 1996), the process is expensive and is used primarily during odor episodes. While most odor problems occur when cyanobacterial populations in the water supply are high, occurrences may be seasonal or even unpredictable. Powdered activated carbon is effective in removing geosmin and MIB from water supplies, but must be used in high concentrations. Granular activated carbon, which often is used in filters at the water treatment plant, is another form of activated carbon that effectively removes geosmin and MIB, but it also is expensive and must be replaced every two or three years.

Dechlorinating Agents

Odor evaluations must examine the overall profile of a water sample. This profile may include contributions from several different odor-causing compounds, including chlorine. Suffet et al. (1994) showed that chlorine produces a masking effect when other odor-causing compounds are present. In some instances, it is desirable to first remove the chlorine so that the other odorous compounds that may be masked by overpowering chlorinous odors can be better quantified. Sensory evaluations generally require approximately 200 mL of sample; therefore, an ideal dechlorinating agent would need to reduce only small amounts of chlorine (2-4 mg/L as Cl₂). While some dechlorinating agents have been used mostly in large-scale industrial applications with high concentrations of chlorine, this does not necessarily ensure their usefulness as dechlorinating agents in taste-and-odor evaluations. An ideal dechlorinating agent would not only effectively remove small amounts of chlorine but it also would have no perceivable odor of its own, not react to produce new odors, and allow detection of underlying odor compounds present in the water sample. Many of the dechlorinating agents identified through a literature review were automatically dismissed from further consideration either because of their inherent odor characteristics, health and safety issues, or possibilities of interaction with the odor compounds themselves. These include activated carbon, ammonia compounds, cyanide, ethylene diamine, formic acid, iodine/iodate, iron compounds, reduced manganese compounds, methane, sodium arsenite, and several sulfur compounds (Appendix A). Dechlorinating agents that were deemed more suited for this study are discussed in the following sections.

Ascorbic Acid. L-ascorbic acid, also known as vitamin C, is a natural reducing agent most often used by medical professionals for removing chlorine from water that is used in kidney dialysis

units (Wiseman 1997). More recently, ascorbic acid has drawn attention for its potential applications as a dechlorinating agent in natural water systems (Peterka 1998). The natural prevalence and associated health benefits of vitamin C make ascorbic acid a safe dechlorinating agent for use in receiving streams contaminated with chlorine. Furthermore, it is safe to handle, does not deplete dissolved oxygen, has little pH effect, and has no inherent odor (Peterka 1998). Ascorbic acid has been shown to effectively reduce chlorine to hydrochloric acid while producing non-toxic dehydro-ascorbate, according to the following equation (Warner and Slayton 1998):

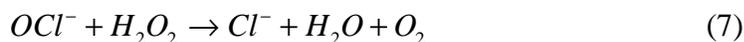


Stoichiometric analysis of the above equation shows that 2.48 mg of ascorbic acid are required to reduce 1 mg of chlorine as Cl_2 :

$$\frac{176.1 \text{ mg } C_6H_8O_6}{\text{mmol } C_6H_8O_6} \times \frac{1 \text{ mmol } C_6H_8O_6}{1 \text{ mmol } Cl_2} \times \frac{1 \text{ mmol } Cl_2}{70.9 \text{ mg } Cl_2} = 2.48 \text{ w/w } C_6H_8O_6 \text{ to } Cl_2$$

Ascorbic acid also reduces chloramines to ammonium chloride (Wiseman 1997) or hydrochloric acid and ammonia (White 1999), depending upon the pH of solution. If chloramines are present, the production of ammonia could interfere with odor evaluations. The safety of ascorbic acid combined with its insignificant pH effect make vitamin C an ideal dechlorinating agent for use during this study.

Hydrogen Peroxide. Hydrogen peroxide has been effectively used for both municipal and industrial wastewater dechlorination (Elizardo 1992; Walsh 1993). It reduces free chlorine to chloride ion (Cl^-), producing oxygen and water, according to the following equation (Mishchenko et al. 1961):



Examination of the stoichiometry of this equation indicates that 0.48 mg of hydrogen peroxide is needed to remove 1 mg free chlorine as Cl_2 (White 1986):

$$\frac{34.0 \text{ mg } H_2O_2}{\text{mmol } H_2O_2} \times \frac{1 \text{ mmol } H_2O_2}{1 \text{ mmol } OCl^-} \times \frac{1 \text{ mmol } OCl^-}{1 \text{ mmol } Cl_2} \times \frac{1 \text{ mmol } Cl_2}{70.9 \text{ mg } Cl_2} = 0.48 \text{ w/w } H_2O_2 \text{ to } Cl_2$$

When used on a large scale, dechlorination with peroxide can be expensive and pose certain risks. Industrial strength solutions contain from 30 percent to 50 percent active ingredient and are highly corrosive. Solutions of 3 percent peroxide (drug-store grade) are safer to handle and better suited for treating small quantities of water. The availability and safety of a 3 percent peroxide solution make it suitable for this study.

Oxalic Acid. For years, oxalic acid has been known as a general reducing agent, lending itself to many analytical and industrial applications. It has been used in the printing and dyeing industries, for bleaching of straw and leather, and for removing paint and rust. Oxalic acid also has been used by industry for pulp and paper processing, in ceramics and pigments, as a metal cleanser, in photography, and in rubber manufacturing (Merck 1983). Gordon et al. (1990) used oxalic acid to eliminate chlorine interference during chlorine dioxide measurements. Oxalic acid reduces chlorine to chloride ion, producing carbon dioxide and hydrochloric acid according to the following equation (Kingston 1999):



Stoichiometric dosing of oxalic acid can be determined by the following equation:

$$\frac{90.0 \text{ mg } (COOH)_2}{\text{mmol } (COOH)_2} \times \frac{1 \text{ mmol } (COOH)_2}{1 \text{ mmol } Cl_2} \times \frac{1 \text{ mmol } Cl_2}{70.9 \text{ mg } Cl_2} = 1.27 \text{ w/w } (COOH)_2 \text{ to } Cl_2$$

Oxalic acid is a colorless, odorless solid that is caustic to human skin, eyes, nose, and throat (OSHA 1999). If ingested, it can cause severe gastric and renal damage (Merck 1983). Although this acid is odorless and effective at reducing chlorine, the associated toxicity of oxalic acid make it less desirable than other dechlorinating agents.

Sodium Nitrite. The nitrite ion (NO_2^-), another well-known universal reducing agent, reduces chlorine to hydrochloric acid while being oxidized to nitrate ion (NO_3^-) according to the following equation (Pontius 1990):



Nitrite is most commonly available as a salt, usually sodium or potassium. The amount of sodium nitrite (NaNO_2) required to reduce 1mg of chlorine as Cl_2 is shown by the following calculation:

$$\frac{69.0 \text{ mg NaNO}_2}{1 \text{ mmol NaNO}_2} \times \frac{1 \text{ mmol NaNO}_2}{1 \text{ mmol HOCl}} \times \frac{1 \text{ mmol HOCl}}{1 \text{ mmol Cl}_2} \times \frac{1 \text{ mmol Cl}_2}{70.9 \text{ mg Cl}_2} = 0.97 \text{ w/w NaNO}_2 \text{ to Cl}_2$$

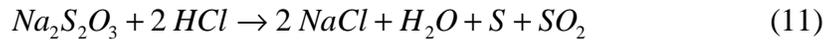
As excess nitrite ion is toxic in natural systems, sodium nitrite has not been used for dechlorination in drinking water supplies.

Sodium Thiosulfate. Unlike some sulfur compounds, sodium thiosulfate is an odorless powder (Merck 1983). Sodium thiosulfate reduces chlorine by a reaction similar to those that occur with other sulfur compounds, but it has been used only experimentally as a wastewater-dechlorinating agent. Sodium thiosulfate has been used widely, however, in the pulp and paper industry and as a bench-scale dechlorinating agent (White 1999). Unfortunately, chlorine reduction with

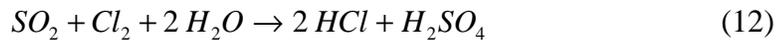
thiosulfate is highly pH and reacts in a stepwise fashion (White 1999). In fact, the following equation is stoichiometric only at pH 2 (White 1999):



While the thiosulfate reaction with chlorine produces bisulfate, excess thiosulfate in the presence of chloride will produce rotten-egg smelling sulfur (Merck 1983):



Sulfur dioxide can then further reduce chlorine, producing sulfuric acid (Connell 1996):



This process implies that exact dosing of thiosulfate is needed to prevent unwanted rotten-egg odors. Therefore, exactly 0.56 mg of sodium thiosulfate are needed to reduce 1 mg of chlorine (as Cl_2):

$$\frac{158.1 \text{ mg } Na_2S_2O_3}{\text{mmol } Na_2S_2O_3} \times \frac{1 \text{ mmol } Na_2S_2O_3}{4 \text{ mmol } Cl_2} \times \frac{1 \text{ mmol } Cl_2}{70.9 \text{ mg } Cl_2} = 0.56 \text{ w/w } Na_2S_2O_3 \text{ to } Cl_2$$

Ultraviolet Light. Many wastewater utilities practice dechlorination to remove excess chlorine from the effluent before it is discharged into natural water supplies. Holding lagoons are one such method of dechlorination where chlorine is degraded over time by natural sunlight. This phenomenon is also observed in swimming pools as residual free chlorine is “burnt-up” over the length of a sunny day. Although decay rates are highly dependent upon weather and climate, chlorine destruction by UV light has been estimated to occur at a rate of 0.75-1.25mg/L per hour between 10 a.m. and 2 p.m., latitude 35°N, June through August (White 1986). This estimate can vary considerably, however, and would require site-by-site evaluations to determine the appropriate contact time.

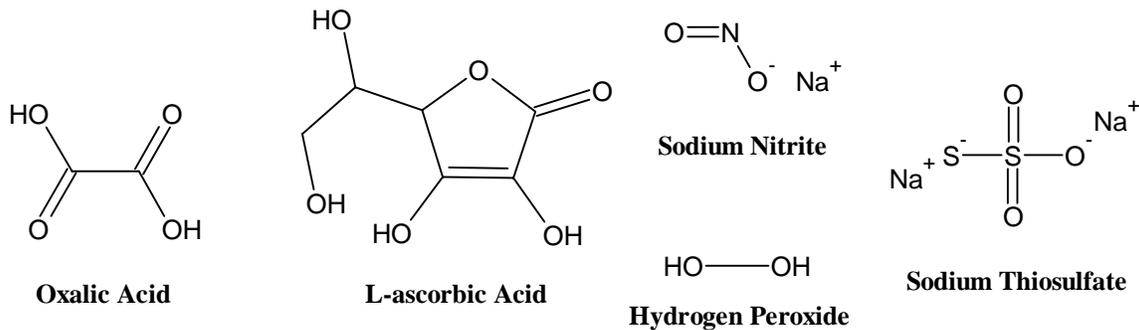


FIGURE 1.3 Chemical structures of selected dechlorinating agents

Odor Evaluation Techniques

Threshold Odor Number. Over the years, many odor-analysis methods have been used to monitor drinking water. The most common is the threshold odor number (TON) test, which, by definition, is the extent of dilution that is required to reduce an odor to a barely perceptible level. The USEPA-established secondary maximum contaminant level (SMCL) for odor in drinking water was defined in terms of a TON of 3. While the TON has been around since the early 1900's, the version used today was first introduced in the 9th edition of *Standard Methods for the Evaluation of Water and Wastewater (Standard Methods)* which was published in 1946 (APHA et al.).

The TON method requires preparation of a series of sample dilutions, and the highest dilution that still produces a barely perceptible odor is used for calculating the TON (Mallevalle and Suffet 1987, APHA et al. 1995). Samples are diluted to 200 mL, heated to 60°C, and presented to panelists in 500-mL Erlenmeyer flasks. The TON is calculated by the following equation:

$$TON = \frac{A+B}{A} \quad (13)$$

where, A = amount of original sample (mL)
 B = amount of dilution water (mL)

While the TON method has remained popular over the years, it presents several problems (Mallevalle and Suffet 1987). First, the TON represents only an overall odor intensity for a particular sample. In reality there may be more than one odorous compound in the sample, but the TON evaluates only the strongest or most volatile component. Second, the TON method produces a number that quantifies the persistence of a compound rather than its actual intensity. Some odor compounds may be more resistant to dilution than others, while not necessarily being present in greater concentrations. Third, the TON test requires many dilutions, which can lead to human error and uncertainty. Finally, the TON shows a lack of good correlation with consumer acceptance; high TON values do not necessarily indicate that a water will be unacceptable to the public.

Flavor Profile Analysis. Largely in response to the discrepancies produced by the TON method, a new method for odor analysis was developed. Within the past decade sensory experts have developed a method which achieves more reproducible results and provides better descriptive data on the overall profile of a sample. Arthur D. Little, Inc. first developed the flavor profile analysis (FPA) method in the late 1940's for the food industry (Cairncross and Sjöstrom 1950). FPA was first used for examining the impact of monosodium glutamate (MSG) addition to processed foods and for solving flavor problems in nutritional capsules (Lawless and Heymann 1999). The method involved training a panel of experts so that they could evaluate several notes, or flavor characteristics, exhibited by one particular food sample and assign intensities to each. The method also allowed for a consensus approach in which panelists

reached a group decision on the characterization of a sample, thus improving the reliability of the data.

In 1981, A.D. Little collaborated with the Metropolitan Water District of Southern California (Metropolitan) to adapt the flavor profile method to the needs of the drinking water field (Krasner et al. 1985). Since then, flavor profile analysis (FPA) has been standardized as a method for drinking water odor analysis (APHA et al. 1995) and is used mainly at larger utilities. In FPA, four to six panelists are trained extensively to recognize and quantify subtle tastes and odors present in a given sample by procedures detailed in the American Water Works Association’s FPA training manual (AWWA, 1993). Odor samples of 200 mL are placed in 500-mL Erlenmeyer flasks, heated to 45°C, then presented to the panelists. The panelists provide descriptions of each odor characteristic in the sample (e.g. chlorine, geosmin), the order in which each was perceived, and the intensity. Often, panelists are provided with a list of common odor descriptors to help in their evaluations. Intensity ratings are based on one of two scales, each widely used:

TABLE 1.2
Flavor Profile Analysis Intensity Scales

1 to 12 Scale ¹)(to 3 Scale ²	
Intensity	Description	Intensity	Description
-	Odor free	0	Odor free
1 or T	Threshold)(Threshold
2	Very weak		
4	Weak	1	Slight
6			
8	Moderate	2	Moderate
10			
12	Strong	3	Strong

¹ adapted from Standard Methods, 1995.

² adapted from Lawless and Heymann, 1999.

At the beginning of each session, panelists are calibrated to one of these scales with a series of taste standards (e.g. sweet or sour). During an actual FPA session, panelists initially evaluate each sample individually and record their results. Once individual assessments have been made, a discussion period is held in which the panel leader elicits each individual's impressions and attempts to group responses together. Panelists may comment during this time so that, together, the group best characterizes the sample.

The flavor profile method improves upon the TON method by using a panel of analysts and formulating consensus recommendations on each sample. Furthermore, an FPA panel can often identify more than one odor component in a water sample, thus generating a better "profile" of the sample's odor character. Like the TON, FPA samples are presented in 500-mL Erlenmeyer flasks, but are heated to 45°C instead of 60°C, making odors slightly less volatile and allowing samples to last longer. The FPA method does however have some problems. Given the consensus/discussion approach used in FPA, data should not be treated independently. Therefore, intensity averages and other statistical analyses are not actually valid although they are often used. Furthermore, strong-willed panelists can influence others and therefore bias FPA results (see sources of error in sensory testing, discussed later). The method also requires intensive training and standardization in order to achieve reliable and reproducible results (AWWA 1993). Lastly, if panels do not follow the same training procedure and testing protocol, data correlation between panels can be difficult and inconclusive.

Quantitative Descriptive Analysis. Similar to the FPA method, but not commonly used in the drinking water field, is the quantitative descriptive analysis (QDA) method, which was

developed in the 1970's by Tragon Corp. (Stone et al. 1974; Stone and Sidel 1992). This method was developed so that statistical analyses could be applied to sensory data; a characteristic not found in the consensus method of FPA (Lawless and Heymann 1999). Like FPA, panelists are selected and trained extensively in a group setting to encourage understanding of the sample standards and intensity scaling. Unlike FPA, testing is then performed individually, without a group discussion at the end. This procedure allows data to be treated as independent and, therefore, analyzed by statistical methods. Furthermore, QDA data are generated by individual panelists, free of influence by a potentially strong-willed panel leader.

In QDA, attribute intensities are evaluated on an unstructured line scale instead of a numerical intensity scale:

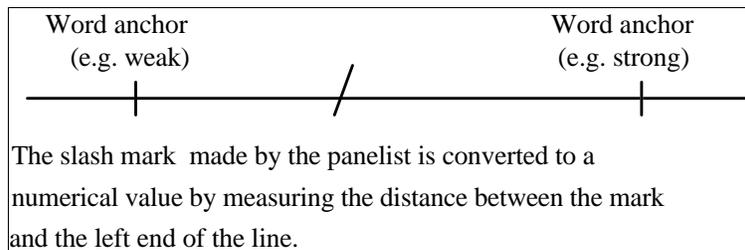


FIGURE 1.4 Unstructured line scale used in QDA.

The scale extension beyond the descriptive anchors helps to encourage panelists to use the full scale (see sources of error in sensory testing, discussed later). Word anchors may be different for each attribute (chlorine or geosmin), and are decided upon by the panel during the initial training sessions. The anchors should be representative of the extreme attribute levels attainable in the item being evaluated (e.g. food or water). Like FPA, panelists use standards representative of the line scale to calibrate themselves before each session.

Panelist marks are converted to a numerical value by measuring their distance from the left extreme of the scale. Since panels create their own scale during testing, average intensities may not be treated as absolute values and thus compared to data produced by another panel. Instead, QDA data are used to compare relative attribute intensities of two or more samples, as evaluated by a single panel. It is especially important that participants in QDA follow a standard sensory protocol, as data are treated independently. This includes coding samples, randomizing the order of presentation, and using individual evaluation booths.

Triangle Testing. The triangle test was first used in the food industry in the Carlsberg breweries and Seagrams distilleries in the 1940's (Helme and Trolle 1946; Peryam and Swartz 1950). The triangle procedure evaluates the overall difference between two samples. Panelists are presented with three samples, two of one product (or drinking water) and one of another. Judges are then asked to identify the odd sample. In the same manner as it was originally used in the breweries, the triangle test is today often used to evaluate the performance of a panelist, that is, how well the panelist can detect small sample differences. In other applications, the triangle test is useful for determining if two samples are noticeably different from one another, but it may be used in this manner only for evaluating overall differences, not individual attribute differences. Panelists participating in triangle testing have only a one-in-three chance of guessing the odd sample. Compared to other discrimination tests with a one-in-two chance of a correct guess, the triangle procedure provides more accurate results on the overall difference of two samples. The comparison procedure of the triangle test makes it very sensitive to small differences between samples. In fact, sample differences are often perceived as much greater than if being evaluated separately by a rating procedure (Lawless and Heymann 1999).

Sources of Error in Sensory Testing

With any sensory testing, one must consider a variety of factors influencing panelist response. A good test design must consider the many sources of error found in sensory testing in order to produce accurate results. The following is a brief list of some errors common to sensory testing:

- Adaptation or fatigue: the decrease in sensitivity experienced when repeatedly exposed to a given stimulus. This factor can be especially detrimental to threshold determination.
- Contrast effect: If a strong sample is presented immediately prior to a weaker sample, the panelist may assign a less-than-normal response to the weaker sample (or possibly none at all).
- Error of central tendency: the subconscious avoiding of extreme ends of evaluation scales. This often occurs when one uses intensity scales because panelists do not tend to use the extreme low or extreme high values of a scale. The error produces a falsely biased central response.
- Expectation error or pattern effect: occurs when a panelist is given too much information about a test, possibly triggering some preconceived notion concerning the sample. For instance, classic threshold tests using ascending concentrations may cause a panelist to expect or anticipate his or her next response before it is actually perceived.
- Logical or stimulus error: a false response invoked by an association with a factor other than the one being evaluated. For instance, a weakening of sample color might cause a panelist to rate its sweetness lower than a sample of more intense color.
- Mutual suggestion: occurs when a panelist is influenced by other members of the panel. This error is especially important and should be considered when using consensus/discussion testing procedures like FPA.
- Presentational errors: caused by the order or manner in which samples are presented to the panelist. Incrementing sample codes (e.g. 1, 2, 3) can cause a panelist to inadvertently rate samples in a biased order.

These and other sources of sensory error have been described in depth elsewhere (Meilgaard et al. 1999; Lawless and Heymann 1999). The sensory tests chosen for this project were evaluated on the basis of their resilience to sensory error as well as their ability to fulfill the project objectives.

Containers for Sensory Testing

Over the years, many different types of sample containers have been used during drinking water odor analyses (Krasner et al. 1985; Krasner 1988; Suffet et al. 1988; APHA et al. 1995). Today, FPA, the most evolved method of evaluation, uses 500 mL wide-mouth glass Erlenmeyer flasks (APHA et al. 1995). Samples in these flasks can be stoppered while in the water bath, thus retaining vapors important to intensity evaluations. Furthermore, samples in the Erlenmeyer flasks can be swirled immediately before the panelists sniff them, thus releasing more molecules into the vapor phase. Unfortunately, analytes of interest can incur odors at the nanogram per liter level, and poorly cleaned glassware can cause unwanted interferences. Furthermore, glass by nature often develops an inherent chalky odor (Krasner et al. 1985). As a result, intensive cleaning is required prior to any sensory testing. The time-consuming process may not be feasible for the on-duty utility operator, especially if multiple samples are being evaluated over his shift (Amoore 1992).

In the past, plastic containers have been recommended as acceptable alternatives to the chalky-smelling glass flasks (APHA et al. 1995). Literature references are unclear as to the type of polymer that is best suited for odor analyses, as many plastics impart strong odors to the sample within. One reference (Meilgaard et al. 1999) recommends using only pretested plastics that have been deemed odor-free and that even then they should not be used in evaluations lasting longer than ten minutes. Another (Mallevalle and Suffet 1987) suggests that 6 or 8 oz. Plastic cups can be used when samples are evaluated at 25°C, but not at the standard 45°C used in FPA.

The origin of these interferences has not been well defined, and limited information regarding the odor characteristics of specific polymers is available because the chemical nature of most products is proprietary. The process by which a plastic is produced, in combination with the resin used, can further affect the odor characteristics of any plastic containers (Schoengood 1997). Some forms of polyethylene food wrapping have been reported to produce odors (Dayton 1993). Philadelphia Suburban Water Authority (Philadelphia suburban) has successfully used both polypropylene specimen cups and Solo cups in their odor analyses (Burlingame 2000). It is possible that one or more types of plastic containers might produce reliable enough results without imparting any noticeable interference on the sample.

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Part II: Interactions Among Various Dechlorinating Agents and Taste-and-Odor Causing Compounds

Article to be submitted to the Journal of the American Water Works Association

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Abstract

In the drinking water field, utilities often need an efficient yet reliable way to detect odorous compounds. Because many utilities use chlorine to disinfect the water, chlorine odors often masks other more subtle odors that may eventually cause consumer complaints. Consequently, odor monitoring at the water treatment plant, where chlorine concentrations are at a peak, may not identify potential displeasing smells. Proper evaluation of these odor-causing substances requires that the chlorine odor first be eliminated before evaluating any remaining odors. Ascorbic acid, hydrogen peroxide, oxalic acid, sodium nitrite, sodium thiosulfate, and ultraviolet irradiation were analytically evaluated for their effectiveness in reducing chlorine. Ascorbic acid, hydrogen peroxide, and sodium thiosulfate were subsequently examined by sensory analysis for their ability to remove chlorinous odors without producing new odors, thus revealing known concentrations of geosmin and MIB.

Keywords: flavor profile analysis, dechlorination, sensory analysis, taste and odor.

Introduction

Although public water supplies are safeguarded by governmental standards, unregulated aesthetically unappealing taste-and-odor problems can be readily apparent to consumers. Taste and odor episodes are most often a result of seasonal algae growth, and, therefore are treated only on an as-needed basis. Consequently, it is important that a utility be able to detect these problematic compounds at extremely low levels so that they can respond before a full-scale taste or odor episode is in progress. Odor monitoring is most often performed by sensory techniques such as flavor profile analysis (FPA), which has been described elsewhere (Krasner et al. 1985, Suffet et al. 1988, APHA et al. 1995).

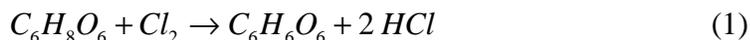
Many water treatment plants disinfect water with chlorine, which can cause strong tastes and odors (Table 2.1). These chlorinous odors often mask other more subtle odors that may eventually cause consumer complaints (Suffet et al. 1994). Especially common are the compounds geosmin and 2-methylisoborneol (MIB), which both cause earthy-musty tastes and odors at nanogram per liter levels. As treated water travels from the water treatment plant to the consumer, the chlorine residual dissipates and may unmask these less-pleasing odors. Consequently, odor monitoring at the utility, where chlorine concentrations are usually at peak levels, may not identify potentially displeasing odors. Proper evaluation of these and other odor-causing substances requires that chlorine interference be removed first. Dechlorinating agents can remove chlorine, but some can either produce unwanted odors or even remove the odorous compounds themselves. The ideal dechlorinating agent is one that effectively removes chlorine but has no perceivable odor of its own, does not create new odors, and, finally, can unmask the odor compounds that potentially can evoke customer complaints. This paper will

examine the effectiveness of several dechlorinating agents in reducing chlorine and subsequent interactions with the odor-causing substances geosmin and MIB.

The technical literature was searched for suitable dechlorinating agents. Many agents were dismissed from further consideration either because of their inherent odor characteristics, health and safety issues, or possibilities of interactions with odor compounds such as geosmin or MIB. These included activated carbon, ammonia compounds, cyanide, ethylene diamine, formic acid, iodine/iodate, ferrous iron compounds, manganous salts, methane, sodium arsenite, and several reduced-sulfur compounds. Six dechlorinating agents were chosen for experimental evaluation on the bases of availability, effectiveness in reducing chlorine, and safety. Stoichiometric doses required for chemical reduction of chlorine are shown in Table 2.2.

Ascorbic acid

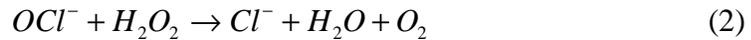
L-ascorbic acid, also known as Vitamin C, is a natural reducing agent used in the medical field for removing chlorine from water used in kidney dialysis units (Wiseman 1997) and as a dechlorinating agent in natural water systems (Peterka 1998). Ascorbic acid is relatively safe, has little effect on pH, and has no inherent odor (Peterka 1998). It effectively reduces chlorine to hydrochloric acid while producing dehydro-ascorbate (Warner and Slayton 1998):



Ascorbic acid also reduces chloramines to ammonium chloride (Wiseman 1997) or hydrochloric acid and ammonia (White 1999), depending upon the pH of solution. If chloramines are present, ammonia production could interfere with odor evaluations.

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) has been effectively used both for municipal and industrial wastewater dechlorination (Elizardo 1992; Walsh 1993). It reduces free chlorine, producing water and oxygen according to the following equation (Mishchenko et al. 1961):



When used on a large scale, dechlorination with peroxide can be expensive and pose certain health risks. Although industrial strength solutions contain from 30 percent to 50 percent active ingredient and are highly corrosive, 3 percent solutions (drug-store grade) are safer and better suited for treating small quantities of water such as those used in this study.

Oxalic acid

Oxalic acid has been widely used a bleaching agent in the pulp and paper industry as well as in the printing and dyeing industries, for bleaching straw and leather, and for removing paint and rust. It also has been used by industry in ceramics and pigments, as a metal cleanser, in photography, and in rubber manufacturing (Merck 1983). Oxalic acid has also been used to eliminate the interference of chlorine in chlorine dioxide measurements (Gordon et al. 1990). Oxalic acid reduces chlorine to chloride ion, producing carbon dioxide and hydrochloric acid (Kingston 1999):



Oxalic acid is a colorless, odorless solid that is caustic to human skin, eyes, nose, and throat (OSHA 1999) and, if ingested, it can cause severe gastric and renal damage (Merck 1983).

Sodium nitrite

Sodium nitrite (NaNO_2), which is another well-known reducing agent, reduces chlorine to hydrochloric acid while being oxidized to nitrate (Pontius 1990):



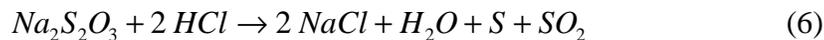
As excess nitrite ion (NO_2^-) is toxic in natural systems, sodium nitrite has not been widely used for dechlorination of wastewaters being discharged to streams or other aquatic systems.

Sodium thiosulfate

Sodium thiosulfate also reduces chlorine and has been used experimentally as a wastewater dechlorinating agent. It has also widely been used in the pulp and paper industry and as a bench-scale dechlorinating agent during analytical measurements (White 1999, APHA et al. 1995). Thiosulfate's effectiveness as a dechlorinating agent is highly pH dependent and reacts in a stepwise fashion (Lind 1995). In fact, the following equation is stoichiometric only at pH 2 (White 1999):



While the thiosulfate reaction with chlorine produces bisulfate, excess thiosulfate in the presence of chloride will produce rotten-egg smelling sulfur (Merck 1983):



UV light

Ultraviolet irradiation has been used for dechlorination at many wastewater utilities before discharged into natural water systems. Natural sunlight dechlorinates chlorinated wastewaters when they are retained in holding lagoons. The same phenomenon also occurs in swimming pools as residual free chlorine is "burnt-up" over the length of a sunny day. Although chlorine-

decay rates are highly dependent upon weather and climate, chlorine destruction by UV light has been estimated to occur at a rate of 0.75-1.25 mg/L per hour between 10 a.m. and 2 p.m., Lat. 35°N, June through August (White, 1986).

The six dechlorinating agents just discussed were evaluated for their efficiency at removing chlorine from aqueous solutions. Those that proved effective were selected for sensory testing by standard odor evaluation protocols adapted from the food industry. Potential interactions of dechlorinating agents with organic odor compounds were evaluated by trained sensory panelists using the triangle test method. These dechlorinating agents were then added to chlorine solutions and evaluated for their effectiveness in reducing chlorinous odors. Additional triangle tests were performed to compare the odors of geosmin, chlorine, and dechlorinating agent dissolved in odor-free water to a sample of geosmin dissolved in odor-free water. The relative intensities of geosmin, MIB, and chlorine in a series of chlorinated and dechlorinated geosmin and MIB samples were also compared by panelists using the flavor profile analysis (FPA) method.

Materials and methods

Reagents. The following chemicals were used over the course of this research project: L-ascorbic acid, A.C.S. grade (CAS 50-81-7; Fisher Scientific, Fair Lawn, NJ), geosmin (CAS 16423-19-1; Sigma, St. Louis, MO), hydrochloric acid, 12.1N A.C.S. grade *PLUS* (CAS 7647-01-0; Fisher Scientific), hydrogen peroxide, 30 percent A.C.S. grade (CAS 7722-84-1; Fisher Scientific), 2-methylisoborneol (CAS 2371-42-8; Supelco, Bellefonte, PA), oxalic acid, 99+% (CAS 144-62-7; Aldrich Chemical, Milwaukee, WI), pH 7 buffer solution, certified ± 0.01 (CAS 7778-77-0, CAS 1310-73-2, CAS 7732-18-5; Fisher Scientific), phenylarsine oxide solution, certified 0.00564N (CAS 637-03-6, CAS 1310-73-2, CAS 7732-18-5; Fisher Scientific), potassium iodide, A.C.S. grade (CAS 7681-11-0; Fisher Scientific), sodium bicarbonate, A.C.S. grade (CAS 144-55-8; Fisher Scientific), sodium nitrite, A.C.S. grade (CAS 7632-00-0; Fisher Scientific), sodium thiosulfate, A.C.S. grade (CAS 10102-17-7; Fisher Scientific), and trans-2-cis-6-nonadienal (CAS 557-48-1; Aldrich Chemical).

Glassware. All glassware used for the odor evaluations was washed in Sparkleen® odor-free detergent (Fisher Scientific), rinsed 10 times with tap water and three times with reagent water. If any odors persisted, cleaning was either repeated or the glassware was steamed with reagent water. All flasks were stored with approximately 200 mL of reagent water in them to prevent formation of chalky odors. Immediately prior to testing, the glassware was again rinsed with reagent water.

I. Dechlorination studies

Amperometric titrimeter. Chlorine concentrations were determined analytically with a Model 172T2012 Fischer & Porter amperometric titrimeter (Capital Controls Company, Inc., Colmar, PA). Samples were titrated at pH 7 with standardized 0.00564N phenylarsine oxide in the presence of excess potassium iodide (APHA et al. 1995).

Sample matrixes. All solutions were prepared with water from a Nanopure ultrapure water system (Barnstead/Thermolyne, model #D4744, Dubuque, Iowa). To ensure against any residual chlorine demand, a sample of Nanopure water was spiked with chlorine to approximately 2 mg/L as Cl₂, and the chlorine residual was monitored over a 7-day period. Samples were kept in 40 mL amber glass vials and stored in the dark to prevent chlorine reduction by light. Analysis of the chlorine residuals showed that no significant chlorine demand existed in the reagent water. All dechlorination studies were performed on chlorine solutions prepared by diluting aliquots of a commercial sodium hypochlorite solution (Clorox®) with reagent water. In all experiments, solutions of the desired chlorine concentration were prepared volumetrically based on amperometric titration of the stock Clorox® solution. Water used in the odor evaluations was

dosed with chlorine at concentrations ranging from 2 mg/L to 4 mg/L as Cl₂, buffered with 50 mg/L alkalinity as CaCO₃, and adjusted to pH 7.

Testing procedure. Dechlorination studies were performed with chlorine solutions that were prepared immediately prior to each test and titrated for determination of the exact chlorine concentration. Samples (250 mL) were then dosed with varying levels of dechlorinating agent and allowed to react while being stirred on a magnetic stir plate for approximately 5 minutes. Stock solutions of each dechlorinating agent (ascorbic acid, oxalic acid, sodium nitrite, and sodium thiosulfate) were prepared by dissolving 5000 mg/L of the salts in reagent water. Dechlorinating agent doses began at the stoichiometric amount needed to reduce the specific amount of chlorine contained in the sample and were incrementally increased so that a dose-response curve based on residual chlorine concentrations could be prepared for each agent. Samples were also monitored for significant pH changes caused by the addition of the dechlorinating agents. Evaluations of UV for dechlorination were conducted by exposing samples in clear, 40-mL glass vials that had been filled with chlorinated samples. The vials were laid flat, side by side, under an ultraviolet lamp (Fisher Scientific, Cat. No. 11-988) with a shortwave bulb, rated at 254nm. The experimental setup was kept in a laboratory cabinet to prevent interference from ambient light. At each time interval, three vials were evaluated for residual chlorine by amperometric titration. In the second trial, the glass vials were replaced with a 1L jar that was kept on a magnetic stir plate to ensure more uniform UV exposure. Samples were withdrawn from the jar at different time intervals and titrated for residual chlorine.

II. Sensory evaluations

Panelists. Thirteen panelists, five males and 8 females, volunteered to participate on an FPA panel. All subjects were either students or faculty in the Environmental Engineering department at Virginia Tech and ranged in age from 21 to 44. Subjects were given no monetary compensation for their participation in this project. Prior to training and testing, panelists were advised not to wear perfumes, hand lotions, scented soaps, or similar products that might interfere with testing. Panelists also were asked to refrain from eating, drinking, or smoking for at least 30 minutes before testing began.

Training. Panelists were trained over a two-day period according to the AWWA manual on flavor profile analysis (FPA) (AWWA 1993). Their ability to identify familiar tastes was evaluated by presenting them with foods such as fruit juice, hot sauce, chocolate, and soy sauce and asking them to note how and where sensations were felt on the tongue. Panelists were taught the seven-point FPA intensity rating scale using sweet, salt, bitter, and sour taste standards. Later, over the course of six to eight hour-long meetings, panelists were taught to use the intensity scale for evaluating the odors of geosmin, MIB, and *trans-2-cis-6-nonadienal* (cucumber) in reagent water.

Sensory testing sessions. All sensory testing was performed in a near-odor-free room. Typical sessions involved the evaluation of from five to seven samples presented in 500-mL Erlenmeyer flasks warmed to 45°C. During triangle test evaluations, panelists were asked to choose the odd sample out of a set of three flasks, two of which contained the same solution. The triangle test provided a one-in-three chance of correctly guessing the odd sample. In order to prevent presentational bias, samples within a set were presented such that all possible combinations were

equally represented. Further sensory testing included a variation of FPA testing. Although panelists were trained according to FPA protocol, sensory evaluations were performed independently, as opposed to the open-discussion manner of typical FPA sessions, so that statistical analyses could be used. During each test session panelists were therefore given individual trays holding their samples and asked to perform their evaluations in a private booth. Samples included several unknowns, odor-free blanks for “cleansing their palettes”, and reference samples (chlorine and/or geosmin) of FPA intensities 4 and 8. Panelist responses were averaged to obtain mean intensity values for each sample.

Results and discussion

I. Dechlorination studies

Figures 2.1-2.6 show the effectiveness of the dechlorinating agents in reducing chlorine. Due to minor variations in the initial chlorine concentration, percent residual chlorine was plotted against the weight-to-weight ratio of dechlorinating agent to chlorine as a means of establishing a common dose-response curve. Ascorbic acid, hydrogen peroxide, and sodium nitrite were effective in eliminating chlorine at dosages within twice the stoichiometric dose. Oxalic acid was not nearly as effective, requiring over 40 times the stoichiometric dose to reduce all chlorine, and caused noticeable pH changes that could potentially alter the odor characteristics of a water sample. While sodium nitrite effectively reduced chlorine, it was eliminated from further testing due to potential health hazard. Although several times the stoichiometric dose of sodium thiosulfate was required to remove all chlorine, it did so quickly and with no significant pH changes. Ultraviolet irradiation proved inadequate for this experiment, as several hours were required to even reduce chlorine levels by 50 percent. For the purposes of this study, a suitable

dechlorinating agent had to remove all chlorine within a few minutes so as to avoid volatilization of the odor-causing compounds. Ascorbic acid, hydrogen peroxide, and sodium thiosulfate were the most suitable and effective dechlorinating agents and, therefore, were chosen for sensory evaluation.

II. Sensory studies

Triangle testing. Triangle testing has been shown to effectively identify small differences among samples (Meilgaard et al., 1999). For this reason, triangle testing was used to determine if solutions of ascorbic acid, hydrogen peroxide, and sodium thiosulfate smelled noticeably different than odor-free water. Each of the dechlorinating agents was added to odor-free, buffered water at concentrations that would have reduced 2 mg/L chlorine, which is a typical concentration encountered during odor evaluations performed at water utilities. Table 2.3 shows, with 95 percent confidence, that none of the three solutions with dechlorinating agent were significantly different than the odor-free sample. In further triangle testing, the panel evaluated the possibility that odors could arise from the reaction between the three dechlorinating agents and chlorine by comparing dechlorinated samples (initial chlorine concentrations of approximately 2 mg/L as Cl₂) to odor-free samples. Sodium thiosulfate immediately produced an apparent rotten-egg odor when it was used to reduce chlorine. The odor of solutions dechlorinated with ascorbic acid and hydrogen peroxide, as before, were not significantly different than odor-free (Table 2.3).

In order to simulate a realistic situation faced by many utility operators, odor evaluations were performed on solutions of 30 ng/L geosmin spiked with 2 mg/L chlorine and subsequently

dechlorinated with ascorbic acid and hydrogen peroxide. The panel compared these samples to one containing 30 ng/L geosmin to determine if either dechlorinating agent could effectively remove all chlorinous odors without altering the odor of a known geosmin concentration. Although amperometric titration showed that both agents were removing chlorine, triangle testing revealed statistically significant odor differences between the chlorinated/dechlorinated sample and the sample containing only geosmin. Panelists indicated that the dechlorinated solutions smelled slightly of chlorine, although the odor was much reduced compared to the solution containing only chlorine. This phenomenon was most likely caused either by vapors or residual chlorine lingering in the headspace or on the glassware. Subsequently, dosing of dechlorinating agent was increased to 10 times that required to reduce the chlorine in hopes that any residual chlorinous odors would be eliminated. Again, significant differences were found among samples (Table 2.3), although panelists communicated that these differences were slight (as the triangle test is designed to detect). Because the differences were suspected as being small, FPA was used to identify the relative perceived intensities for geosmin and chlorine in these samples.

FPA analyses. In the FPA sessions, panelists were asked to evaluate and rate samples for both geosmin and chlorine. Before each test session, panelists were calibrated with geosmin and chlorine standards. Weber-Fechner plots for geosmin and chlorine in odor-free water were developed and compared to previous threshold values (Figures 2.7 and 2.8), as a means of validating the panel's performance. Geosmin thresholds (in odor-free water) were found to be between 7 ng/L and 12 ng/L, which is consistent with thresholds of 6 ng/L to 10 ng/L reported in the literature (Mallevalle and Suffet 1987, Rashash et al. 1997). Panelists also showed good

correlation and repeatability in the geosmin evaluations. They identified chlorinous odors at levels slightly greater than 0.1 mg/L as Cl₂ (at pH 7), which is less than the threshold values shown reported by Krasner and Barrett (1984) (Table 2.1).

Once Weber-Fechner plots were generated, panelists were presented with four unknown samples: one containing only geosmin at 30 ng/L; one containing 30 ng/L geosmin and chlorine at 1 mg/L; a chlorinated geosmin sample that had been dechlorinated with ascorbic acid at 10 times the effective reducing dose (30 mg per mg Cl₂); and, finally, another chlorinated geosmin sample that had been dechlorinated with hydrogen peroxide at 10 times the effective reducing dose (6 mg per mg Cl₂). Results clearly showed the masking effect chlorine had on the perceived intensity of geosmin (Figure 2.9). Panelists rated the geosmin odor intensity strongest in the geosmin-only sample (FPA intensity 4.1) and weakest in the chlorinated geosmin sample. In fact, panelists rated the chlorinated geosmin sample as having almost no geosmin odor at all (FPA intensity 0.5), even though both samples contained 30 ng/L geosmin. Furthermore, while ascorbic acid and hydrogen peroxide did not eliminate the chlorine aroma, they clearly reduced the perceived intensity of chlorine without affecting the perceived geosmin intensity. Panelists rated the chlorine intensity highest in the chlorinated geosmin sample (FPA intensity 8.5), while they rated the chlorine odor in the two dechlorinated samples closer to FPA intensity 2.

This same procedure was repeated for chlorinated and dechlorinated MIB samples. Similar results were seen; both ascorbic acid and hydrogen peroxide aided in reducing chlorinous odors, thus revealing underlying MIB odors (Figure 2.10).

Conclusions

- Oxalic acid was inefficient as a dechlorinating agent, requiring over 40 times the stoichiometric dose to reduce small amounts of chlorine. Ultraviolet irradiation also proved ineffective as a relatively rapid way to dechlorinate water, producing average chlorine reductions of 0.18-0.26 mg Cl₂/L/hour.
- Sodium thiosulfate produced a rotten egg odor when used in excess to reduce chlorine, implying that some byproduct of the reduction reaction forms in the presence of excess thiosulfate. This problem makes sodium thiosulfate unsuitable as a dechlorinating agent for odor evaluations, as over-dosing and production of the rotten-egg odor can easily occur in laboratory situations.
- Triangle tests showed that while ascorbic acid and hydrogen peroxide reduced chlorine, they did not completely remove chlorinous smells even when chlorine could not be detected by amperometric titration. This phenomenon may be attributed to chlorinous vapors either trapped in the flask or absorbed on the flask walls.
- Flavor profile analysis data showed that ascorbic acid and hydrogen peroxide eliminated the masking effect of chlorine on geosmin and MIB. Both dechlorinating agents reduced chlorinous odors and increased the perceived intensity of geosmin and MIB. Both ascorbic acid and hydrogen peroxide, therefore, would be equally effective as dechlorinating agents during sensory analyses of drinking water containing organic odor compounds of similar chemical structure to geosmin or MIB.
- Only through months of practice and experience in detecting small sample differences in the triangle tests were panelists able to effectively use the FPA scale and evaluate more than one odor characteristic in a single sample. Even after panelists had been practicing almost one year, performance was highly dependent on the order of presentation of samples and the number that were presented in a single session.
- Odor threshold concentrations generated in this research for both geosmin and chlorine agreed with previously reported threshold values.

TABLE 2.1
Chlorine Odor and Taste Thresholds

Compound	pH	Odor Threshold (mg/L as Cl ₂)	Taste Threshold (mg/L as Cl ₂)
Hypochlorous acid	5.0	0.28	0.24
Hypochlorite ion	10.0	0.36	0.30
Monochloramine	8-9	0.65	0.48
Dichloramine	4.0	0.15	0.13

(adapted from Krasner and Barrett 1984)

TABLE 2.2
Stoichiometric Dosages of Dechlorinating Agents

Dechlorinating agent	Stoichiometric dose (mg agent per mg chlorine as Cl ₂)	Effective dose as determined by this research (mg agent per mg chlorine as Cl ₂)
Ascorbic acid	2.48	3.0
Hydrogen peroxide	0.48	0.6
Oxalic acid	1.27	45.0
Sodium nitrite	0.97	1.1
Sodium thiosulfate	0.56	2.2

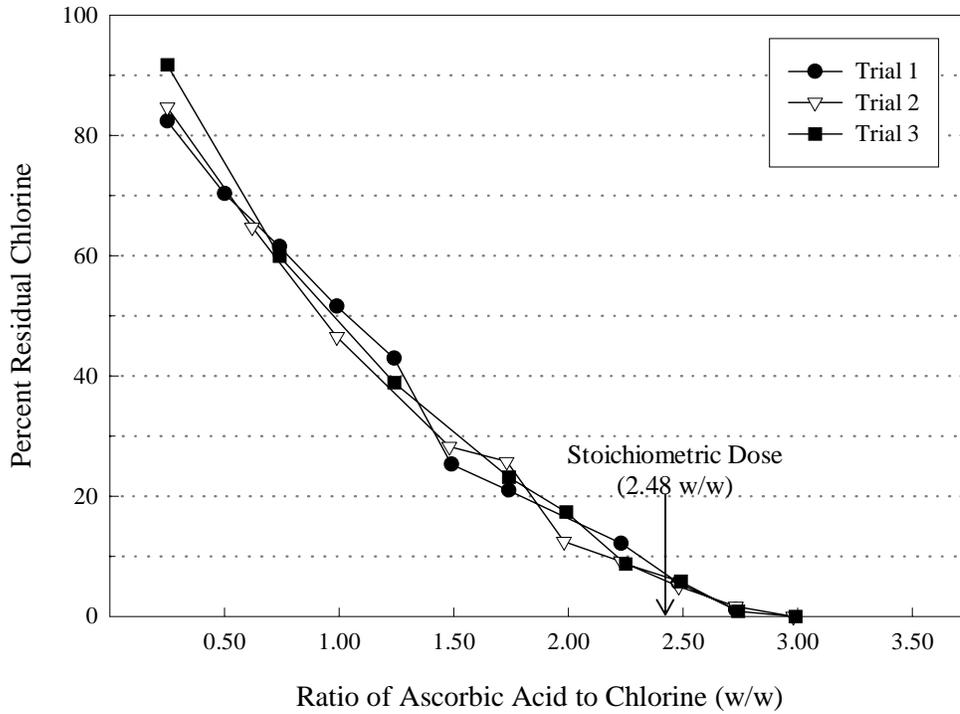


FIGURE 2.1 Reduction of aqueous chlorine solutions by L-ascorbic acid. Experiments were performed on solutions of 2-4 mg/L as Cl_2 , at pH 6.5-7, and allowed to react approximately 5 minutes at room temperature.

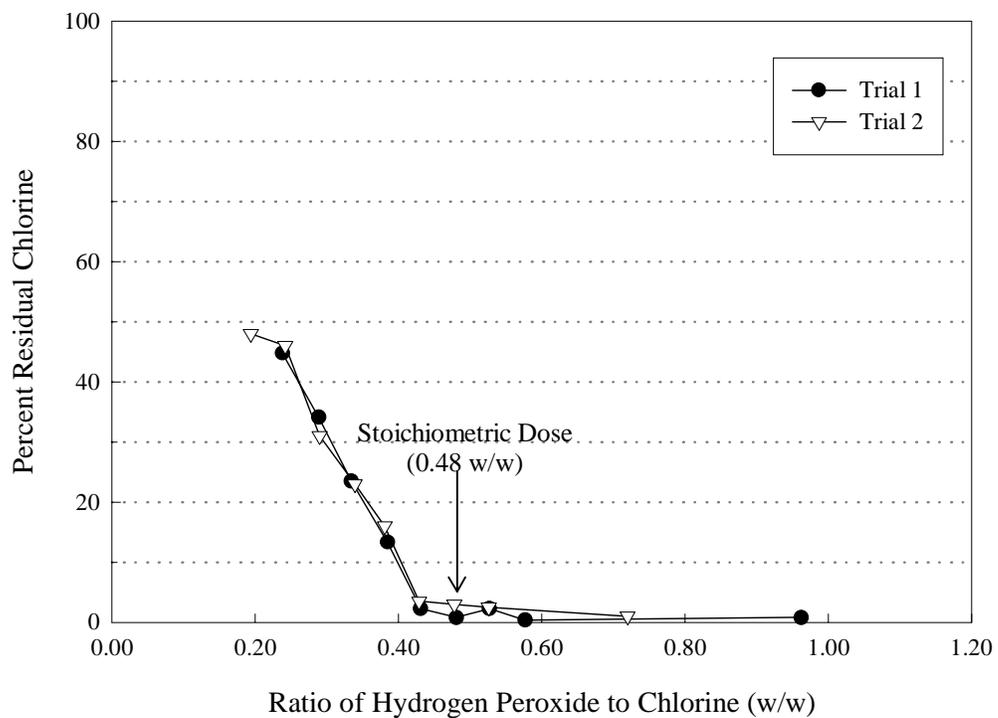


FIGURE 2.2 Reduction of aqueous chlorine solutions by hydrogen peroxide. Experiments were performed on solutions of 2-4 mg/L as Cl_2 , at pH 6.5-7, and allowed to react approximately 5 minutes at room temperature.

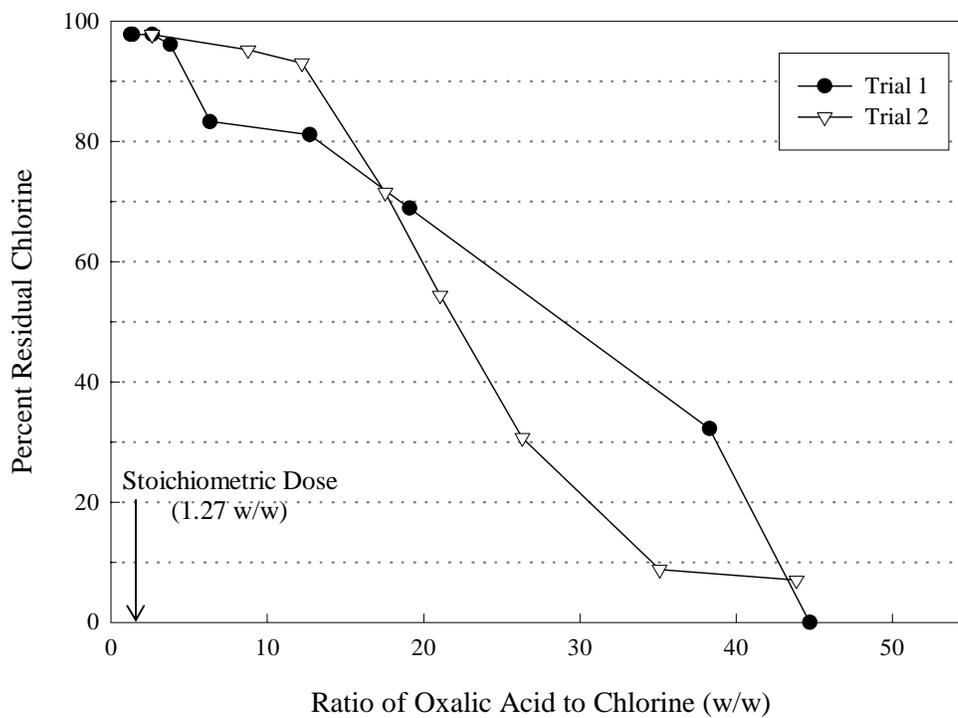


FIGURE 2.3 Reduction of aqueous chlorine solutions by oxalic acid. Experiments were performed on solutions of 2-4 mg/L as Cl_2 , pH 6.5-7, and allowed to react approximately 5 minutes at room temperature.

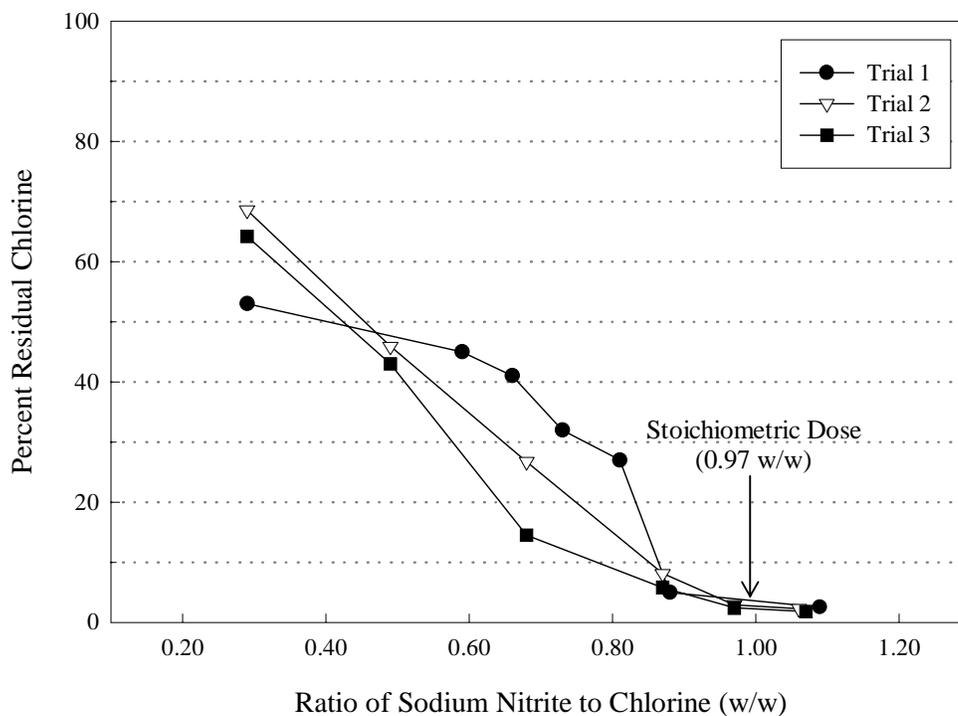


FIGURE 2.4 Reduction of aqueous chlorine solutions by sodium nitrite. Experiments were performed on solutions of 2-4 mg/L as Cl_2 , at pH 6.5-7, and allowed to react approximately 5 minutes at room temperature.

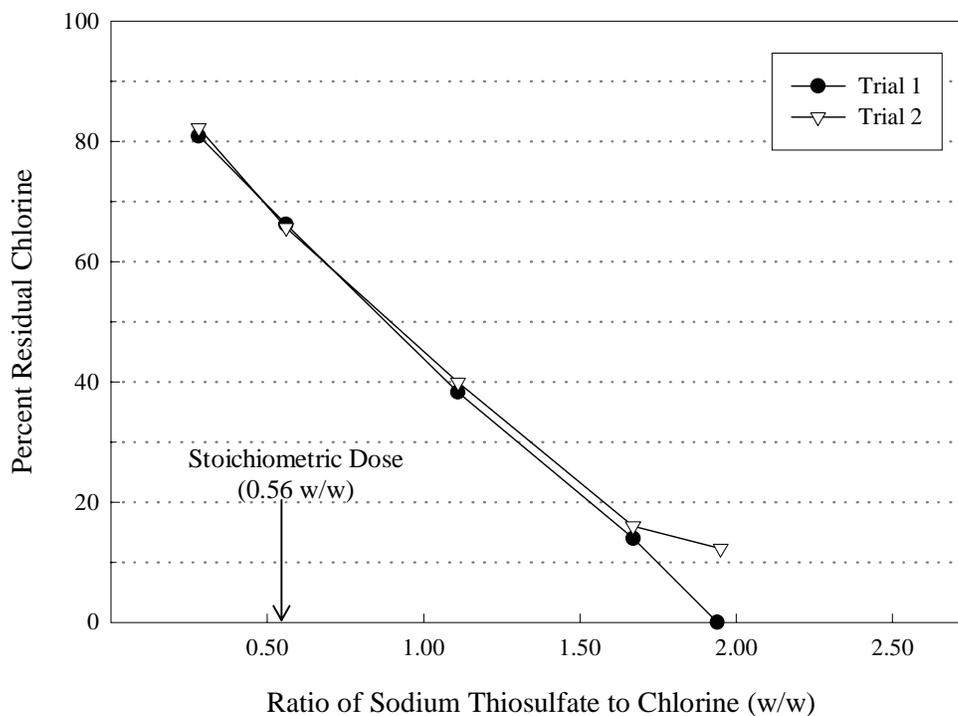


FIGURE 2.5 Reduction of aqueous solutions of chlorine by sodium thiosulfate. Experiments were performed on solutions of 2-4 mg/L as Cl_2 , at pH 6.5-7, and allowed to react approximately 5 minutes at room temperature. Stoichiometric dose is accurate only at pH 2 (White 1999).

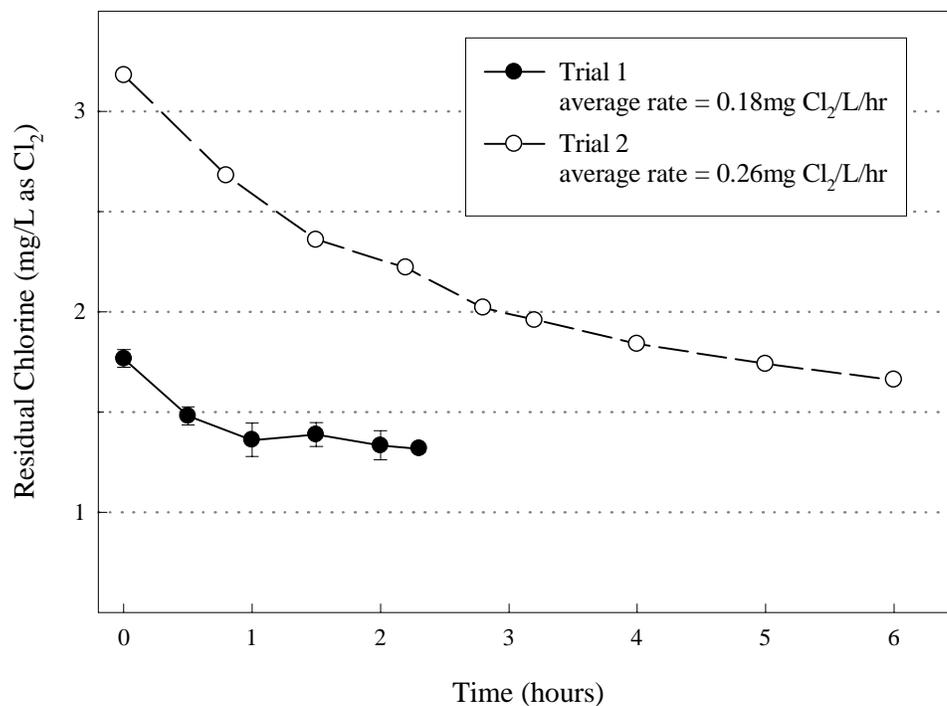


FIGURE 2.6 Reduction of aqueous chlorine solutions by ultraviolet light. Experiments were performed on solutions of 2-4 mg/L as Cl₂, at pH 6.5-7, and placed under a 245 nm shortwave bulb at room temperature.

TABLE 2.3
Summary of Triangle Testing¹

Test description	Dechlorinating agent	Dose ratio of dechlorinating agent to chlorine (w/w)	Number of correct responses / total responses	Critical value needed for significance ($\alpha = 0.05$) ²	Significant?
Odor free water vs. aqueous solutions of dechlorinating agent	ascorbic acid	3.0	6/19	11	NO
	hydrogen peroxide	0.6	7/20	11	NO
	sodium thiosulfate	2.5	9/20	11	NO
Odor free water vs. solution of [Cl ₂ + dechlorinating agent]	ascorbic acid	3.0	5/16	9	NO
	hydrogen peroxide	0.6	8/16	9	NO
	sodium thiosulfate	2.5	10/13	8	YES
Geosmin solution ³ vs. solution of [Cl ₂ + dechlorinating agent + geosmin]	ascorbic acid	3.0	13/18	10	YES
	hydrogen peroxide	0.6	10/18	10	YES
Geosmin solution ³ vs. solution of [Cl ₂ + dechlorinating agent + geosmin]	ascorbic acid	30.0	12/18	10	YES

¹Experiments were performed with 10-12 panelists using samples buffered with 50 mg/L as CaCO₃, at pH 7 and heated to 45°C.

²Panelists performed each test twice.

³Critical value obtained from Table T8 (Meilgaard et al., 1999), based on number of observations and alpha level of 0.05.

⁴Geosmin present at 30 ng/L

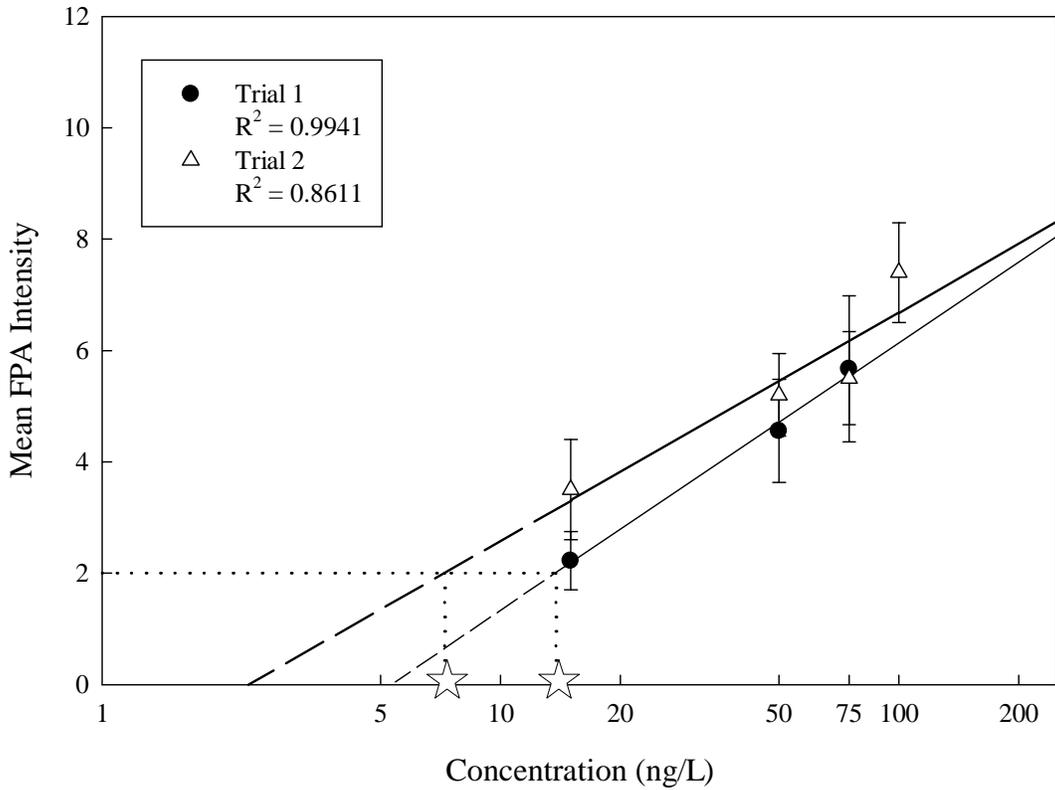


FIGURE 2.7 Weber-Fechner plots for geosmin. Dashed lines represent theoretical extension of W-F lines beyond those concentrations evaluated by panelists. Experiments were performed with 10-12 panelists using geosmin samples, presented in Erlenmeyer flasks and heated to 45°C. Evaluations were performed on different days, using reference samples of intensity “8” (100 ng/L) and “4” (30 ng/L). Stars indicate odor threshold concentration (OTC).

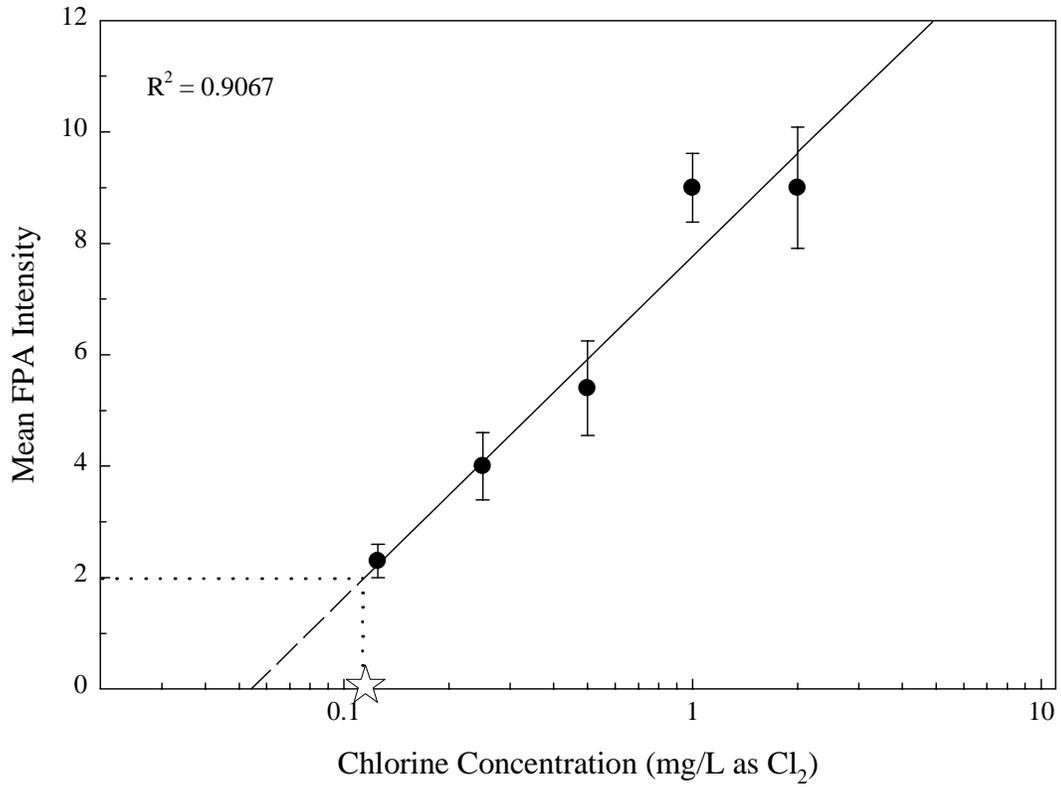


FIGURE 2.8 Weber-Fechner plot for chlorine. Dashed lines represent theoretical extension of W-F line beyond those concentrations evaluated by panelists. Experiments were performed with 10-12 panelists using chlorine samples, presented in Erlenmeyer flasks and heated to 45°C. Star indicates odor threshold concentration (OTC).

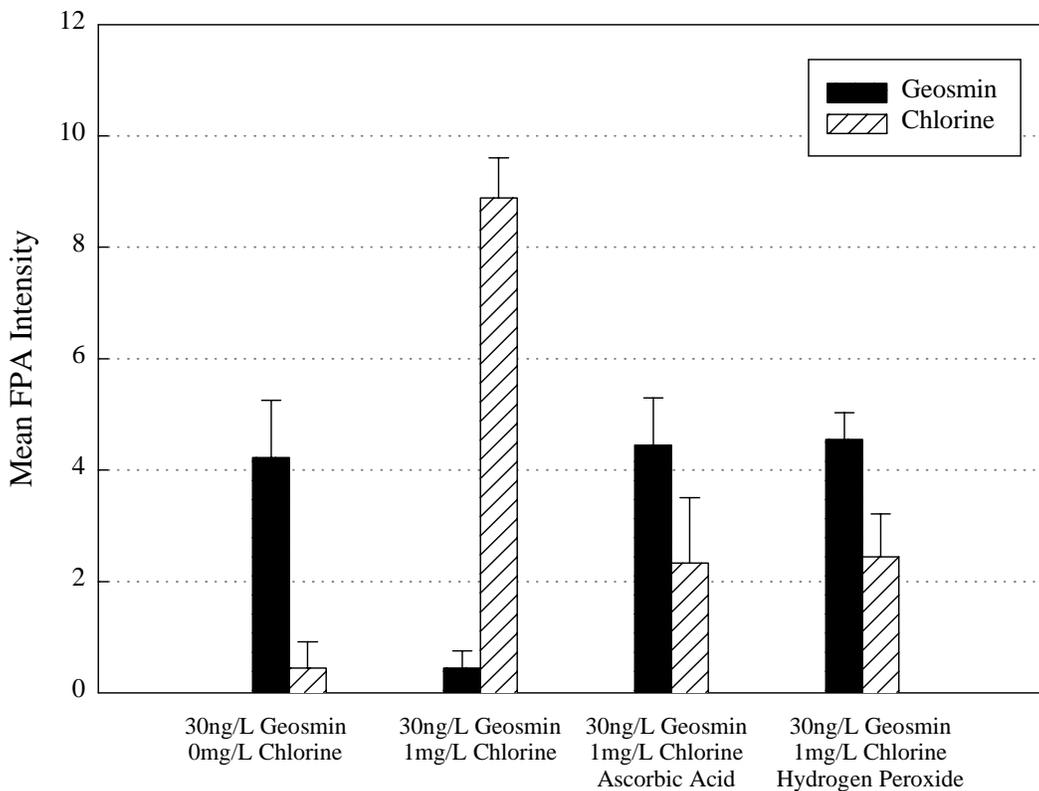


FIGURE 2.9 FPA evaluations of (a) geosmin only; (b) geosmin plus chlorine; (c) geosmin, chlorine, and ascorbic acid; and (d) geosmin, chlorine, and hydrogen peroxide. Experiments were performed with 10-12 panelists, using samples presented in Erlenmeyer flasks and heated to 45°C.

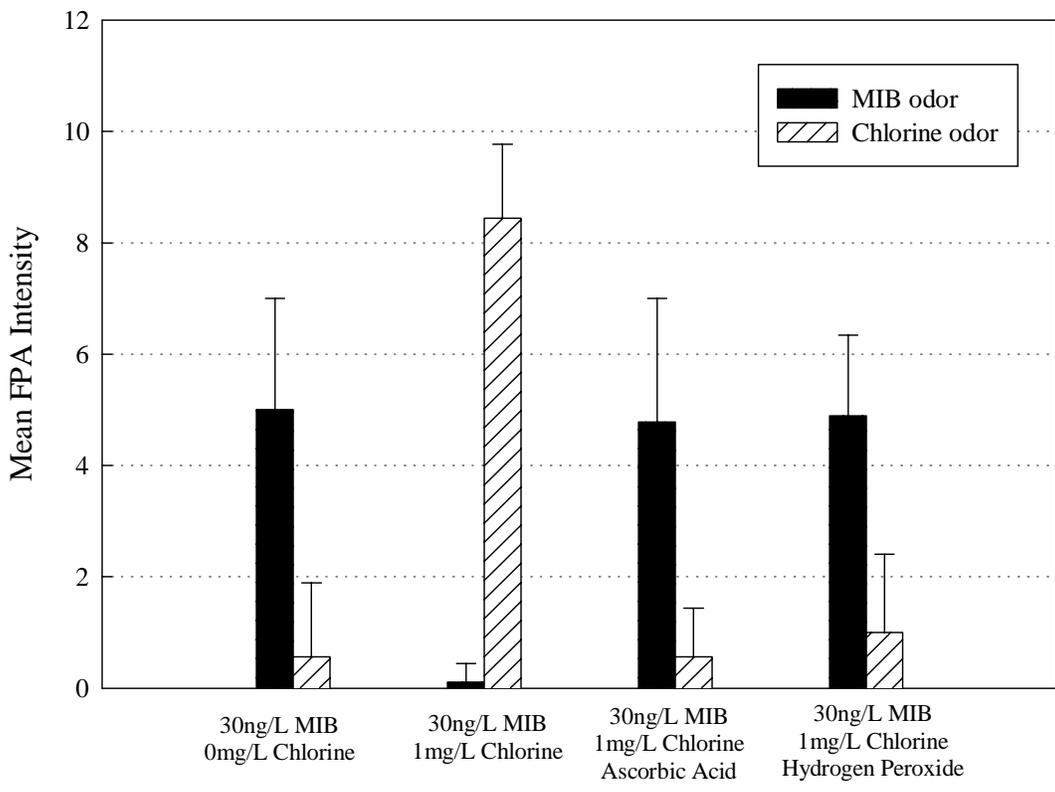


FIGURE 2.10 FPA evaluations of (a) MIB only; (b) MIB plus chlorine; (c) MIB, chlorine, and ascorbic acid; and (d) MIB, chlorine, and hydrogen peroxide. Experiments were performed with 10-12 panelists, using samples presented in Erlenmeyer flasks and heated to 45°C.

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Part III: Investigation of the Sensory Attributes of Alternative Containers for use in Drinking Water Odor Analysis

Technical paper to be submitted to the Journal of the American Water Works Association

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Abstract

In the drinking water field, utilities often need an efficient yet reliable way to detect odorous compounds. The most common odor-analysis methods (TON and FPA) involve the use of glass flasks, which often either develop chalky odors or have persistent lingering odors from previous evaluations. Furthermore the glass flasks break easily and are difficult to clean. The research described in this paper evaluated the suitability of four types of disposable plastic containers for odor analyses. Panelists ranked the inherent cup odors by smelling odor-free water placed in them. Several clear plastic cups were deemed odor-free and were filled with an odorant cocktail; the odor of these were then compared by a multiple-comparison procedure to the odor of solutions in 500-mL wide-mouth glass Erlenmeyer flasks currently used by the drinking water industry. Odors of samples in clear plastic cups did not differ significantly from those in Erlenmeyer flasks, but FPA testing showed that odors of samples contained in larger (500-mL), clear high-impact polystyrene plastic cups (DART®) were more nearly equivalent to those of solutions contained in Erlenmeyer flasks when analyzed using geosmin-only solutions.

Keywords: drinking water, disposable or plastic cups, odor, flavor profile analysis, geosmin

Introduction

In the drinking water industry, odor evaluations are often performed on water samples many times over the course of a day. Furthermore, the on-duty utility operator may occasionally be the only person involved in the evaluations. As a result, the operator may be performing many different evaluations during the shift and, therefore, needs an efficient and economical, yet reliable, way to detect the presence of odorous compounds. Over the years, different sensory methods have been developed that require the use of many types of containers, including various sizes of plastic cups and large glass flasks (Krasner et al. 1985, Krasner 1988, Suffet et al. 1988, APHA et al. 1995). The threshold odor number (TON) test (Method 2150B, APHA et al. 1995) and flavor profile analysis (FPA) (Method 2160D, APHA 1995) require evaluation of 200 mL samples presented in 500-mL wide-mouth glass Erlenmeyer flasks. The Erlenmeyer flasks are favored because they can be stoppered while in the water bath, and panel can swirl samples without spilling them immediately prior to sniffing. The swirling technique helps to release odor molecules into the vapor phase and, thus, into the nose. Because many analytes of interest can cause odors at the nanogram per liter level, improper cleaning of the glassware can cause unwanted interferences. Furthermore, glass often has an inherent chalky odor (Mallevalle and Suffet 1987). As a result, intensive cleaning is required prior to any sensory testing (Mallevalle and Suffet 1987). This time-consuming process may not be feasible for the on-duty utility operator, especially if multiple samples are being evaluated over one shift (Amoore 1992).

Disposable plastic containers have been used widely for taste testing in the food industry. Some disposable containers have been used for odor analyses, but some odor interferences have been noted (Mallevalle and Suffet 1987). Generally the decision has been left to each individual odor

panel to decide if disposable cups provide undesirable background interference (Mallevalle and Suffet 1987, APHA et al. 1995). The origin of these interferences has not been well defined and there is limited information available on the odor characteristics of specific polymers (Dayton 1993, Tershansy and Cornell 1999).

The objectives of this project were to examine the odor characteristics of several commercial disposable plastic containers, compare their odor properties to the 500-mL wide-mouth Erlenmeyer flask, and determine which disposable container could be used in drinking water odor testing (Table 3.1).

Materials and methods

General approach. A ranking procedure was used to test the odor similarities among water samples contained in three types of plastic cups and a glass beaker, all of similar dimensions (Table 3.2). Experimental differences among containers were identified by a least significant difference test (LSD). This procedure was useful in identifying any odor characteristics inherent to the containers themselves. Containers that had no significant odor characteristics were then tested against the 500-mL wide-mouth Erlenmeyer flask by a multiple comparison procedure. Containers were filled with a known odorous “cocktail” sample, and a multiple comparison procedure was used to determine which, if any, disposable container could produce an odor intensity not significantly different from the standard 500-mL Erlenmeyer flask. Finally, FPA was used to compare odors of geosmin-containing solutions contained in larger (500-mL) non-odorous clear plastic containers to those contained in 500-mL Erlenmeyer flasks using geosmin as the sample matrix.

Product specifications. The following chemicals were used over the course of this project: geosmin (CAS 16423-19-1, Sigma, St. Louis MI), 2-methyisoborneol (MIB) (CAS 2371-42-8, Supelco, Bellefonte PA), and *trans-2-cis-6-nonadienal* (CAS 557-48-1, Aldrich, Milwaukee WI). Odor-free water was obtained from a Nanopure ultrapure water system (Barnstead/Thermolyne, model #D4744, Dubuque IA).

Opaque polystyrene plastic cups (Solo® 9 oz.), translucent clear K-resin plastic cups (Kroger-brand® 7 oz.), milky polypropylene plastic specimen cups with polyethylene lids (Fisherbrand® 8 oz., Cat. No. 11-838-21) and translucent clear high-impact polystyrene cups (DART® 500 mL) were used for odor analyses (Table 3.2). Plastic cups were covered with clean watch glasses to entrap water vapor. Cups were not washed prior to testing and were used only once.

Glass containers included 250-mL beakers and 500-mL wide-mouth Erlenmeyer flasks. All glassware was washed using Sparkleen® (Fisher Scientific, Milwaukee, WI) odor free detergent, steamed with odor-free water, and stored with odor-free water to prevent the development of chalky odors (AWWA 1993).

Testing environment. Sensory testing was performed in the New Engineering Building and Norris Hall, both on the Virginia Tech campus. Space limitations, combined with the large amounts of glassware needed and the necessity of a water bath, made ideal sensory testing conditions impossible. However, testing was performed in near odor-free rooms and controlled so that panelists were not influenced by one another. Testing was conducted over several days and water samples were prepared fresh on the morning of each test day.

Selection of panelists. A total of 50 unpaid panelists, all of whom signed informed consent forms, were used for each of the ranking and multiple comparison procedures. Panelists included nearly equal numbers of males and females, all between the ages of 20 and 50. Forty panelists were untrained while 10 had been previously trained according to the FPA training manual (AWWA 1993) and had worked together for the previous ten months on drinking water odor evaluations. Only the trained panelists participated in FPA testing.

Simple ranking test. A ranking test was used to identify any inherent odors among the smaller sized plastic disposable cups (Meilgaard et al. 1999). Each panelist received three plastic containers (the opaque plastic Solo cup, the milky plastic specimen cup, and the translucent clear Kroger cup) and a 250-mL glass beaker, filled with varying amounts of odor-free water heated to 45°C and covered with clean watch glasses. The order of presentation of cups was randomized and balanced so that all 24 possible container combinations were equally represented. The volume of water placed in the containers was varied so that the surface area-to-volume ratio would be the same in each (Table 3.2). For this reason, a 250-mL glass beaker was used instead of the Erlenmeyer flask to ensure that the background odors caused by the plastics were being evaluated rather than the effects of container sizes and shapes, a phenomenon later investigated in the multiple comparison procedure. Odor-free water was added to the containers so that only the container would contribute to the background odors perceived by the panelists.

Panelists were asked to rank the odors they perceived in these containers from 1 to 4 in order of increasing odor intensity, with 4 being the most odorous (see Figure 3.1 for sample scoresheet).

Statistical analyses identified which plastic containers were significantly different from the assumed odor-free glass beaker.

Multiple comparison test. Next, a multiple comparison test was performed to compare the odor-free containers to the commonly used 500-mL wide-mouth glass Erlenmeyer flask (Meilgaard et al. 1999). Not only were the effects of plastic containers on odor perception evaluated but also the effects of the container sizes and shapes as well. Odors of samples contained in glass beakers were also compared to those in Erlenmeyer flasks so that potential differences between container shapes could be evaluated. Panelists were given a reference sample (in the 500-mL Erlenmeyer flask) and samples in three test containers (the opaque Solo cup, the translucent clear Kroger cup, and the 250-mL beaker). Since these containers had already been deemed odor-free during the ranking procedure, an odorous sample matrix was needed for comparison. Each container was filled with a “cocktail” of odor-free water spiked with 30 ng/L each of geosmin, MIB, and nonadienal and presented to the panelists. Three odor compounds were included in the cocktail so that panelists who might be anosmic to one of the compounds could still identify odor differences.

Panelists were asked to rate the odor intensity of the sample in each test container as either greater than or less than the odor intensity of the sample in the reference Erlenmeyer flask (see Figure 3.2 for sample scoresheet). The objective of this test was to determine whether the odor intensities of the cocktail in the test containers and Erlenmeyer flask were significantly different from each other. Furthermore, when a difference did exist, direction could be established as to whether test containers produced more or less-intense responses than the Erlenmeyer flask. As

in the ranking test, this procedure was performed over several days, and fresh cocktails were prepared each test day.

Flavor profile analysis. Typical FPA sessions involved the evaluation of from four to seven geosmin samples presented to the panelists in 500-mL translucent clear DART® cups and 500-mL wide-mouth glass Erlenmeyer flasks. FPA evaluations were performed independently (without a consensus approach) so that statistical analyses could be used. Panelists were given several geosmin samples ranging in concentration from 0 ng/L to 100 ng/L, odor-free blanks for cleansing their palettes, and reference geosmin standards at FPA intensities 4 (15 ng/L) and 8 (100 ng/L), which are values obtained from prior research (Mallevalle and Suffet 1987).

Testing was performed on three separate days. During the first FPA session panelists were presented with the two geosmin reference standards in Erlenmeyer flasks; they then rated geosmin odor intensities in six unknown samples. Three of the unknown samples were presented in 500-mL Erlenmeyer flasks, and the other three in 500-mL translucent clear plastic DART® cups. During the second session, panelists were again given geosmin reference standards in 500-mL Erlenmeyer flasks; they then evaluated the odor intensity of geosmin in four unknown samples, all presented in 500-mL Erlenmeyer flasks. Finally, in the third session, panelists were presented with geosmin reference standards in the 500-mL clear plastic DART® cups and asked to evaluate the geosmin odor intensity of four unknown samples, also presented in 500-mL clear plastic DART® cups. Responses from the 10 panelists were averaged to obtain mean intensity values for each sample; these values were then used to create several Weber-

Fechner plots for geosmin. Odor threshold concentrations (OTCs) were identified from these plots at concentrations corresponding to an FPA intensity of 2.

Statistical approach. Because the ranking and multiple comparison procedures were used to test for similarity, alpha and beta errors were both strongly considered. In other words, this project aimed to prove that samples in all the test containers smelled the same as those presented in the currently used 500-mL wide-mouth Erlenmeyer flasks. For this reason, it was important to minimize the risk of claiming a difference among containers when none truly existed (a false positive or alpha error). Equally important (as is true for any sensory research) was minimizing the risk of missing differences between containers when they actually did exist (a false negative or beta error). Because both these errors were important to this project, both the alpha and beta error evaluations were preset at 0.05 each. The ranking data were subjected to a Friedman analysis to determine if any differences in perceived odor intensities existed amongst containers (Meilgaard et al. 1999). When a significant difference was found, a multiple comparison was used to determine specific relationships among containers (Meilgaard et al. 1999). Data from the multiple comparison procedure were converted to a 9-point scale (see Figure 3.2) and analyzed by a one-way analysis of variance (ANOVA) (Larmond 1977). When significant differences were found, a Tukey comparison was used to determine which containers differed from the rest (Larmond 1977). Logical assumptions could then be made concerning the relative order of perceived odor intensity induced by each container.

Because FPA data was collected independently, instead of by the usual consensus method, geosmin intensity data could be treated independently and, therefore, analyzed by standard

statistical procedures. Means were calculated from each set of data and plotted along with their associated standard errors.

Results and discussion

Results from the simple ranking procedure showed, with 95 percent confidence, that once-odor-free water in the Fisherbrand® milky plastic cup smelled significantly stronger than water in the other three containers (Table 3.3). Furthermore, the odor intensities of samples in the presumed odor-free glass beaker were statistically the same as those contained in the opaque plastic Solo® cups, and the intensities of samples in both containers were statistically greater than those in translucent clear Kroger® cups. Based on these results, the null hypothesis was rejected and the Fisherbrand® milky plastic cups were deemed too odorous and thus were eliminated from further testing.

Next, cocktail samples in the opaque plastic Solo® cups, translucent clear plastic Kroger® cups, and 250-mL beakers were compared to samples in the 500-mL Erlenmeyer flasks by a multiple comparison procedure. Multiple comparison data showed with 95 percent confidence, that the perceived intensities of the odorant cocktails in the test containers were no different than those in the standard 500-mL Erlenmeyer flasks (Table 3.4).

Although multiple comparison results showed no significant difference among containers, it was noted that the ten trained panelists all found the odor intensity of the cocktail in the Erlenmeyer flask to be much stronger than those in the test containers. For this reason, an FPA procedure was used to generate odor threshold data for geosmin in order to test the similarities between a

larger-sized (500-mL) high-impact polystyrene cup (DART®) and the 500-mL Erlenmeyer flask (Table 3.2). FPA data showed that when given geosmin reference standards in Erlenmeyer flasks and asked to rate a series of geosmin samples in both Erlenmeyer flasks and high-impact polystyrene cups, the Erlenmeyer samples showed higher average odor intensities (Figure 3.1A). While panelists could identify geosmin at concentrations as low as 5 ng/L in both containers, higher concentration samples were harder to identify when they were presented in the wider mouth cups. During the next exercise, panelists were given a series of geosmin reference standards in polystyrene cups and asked to evaluate a series of geosmin samples also presented in the disposable cups. The following day, panelists repeated the procedure but were given reference standards in Erlenmeyer flasks and asked to evaluate only samples presented in Erlenmeyer flasks. Data from these two test sessions were plotted against each other on the same graph (Figure 3.1B). The resulting Weber-Fechner plots were much more similar in slope and geosmin odor threshold than the plots generated using only Erlenmeyer reference standards (Figure 3.1).

Conclusions

- Some plastic cups are inherently more odorous than others and should not be used for drinking water odor analysis. Odors imparted to water samples in polypropylene milky plastic specimen containers (Fisherbrand®) were significantly stronger than those in clean 250 mL glass beakers.
- No significant differences were found in the odor intensity of cocktail samples (15 ng/L each of geosmin, MIB, and nonadienal) presented at 45°C in odor-free plastic containers (K-resin and polystyrene), 250 mL glass beakers, and 500 mL glass Erlenmeyer flasks, all at the same sample volume-to-headspace ratio.
- FPA evaluations of geosmin samples in 500 mL clear plastic DART® cups (high-impact polystyrene) showed similarity to evaluations of geosmin in 500 mL glass Erlenmeyer flasks, when reference standards were presented in the same type of container as the samples. Therefore, 500 mL clear plastic DART® cups of high impact polystyrene may be used for

odor evaluations of geosmin so long as panelists are provided with geosmin reference standards also in the plastic cups. This conclusion applies only to evaluations of geosmin-containing samples, and its extension to samples containing other odorous organic compounds requires additional testing.

TABLE 3.1
Summary of Sensory Test Objectives

Sensory Test	Objectives	Null Hypothesis
Simple Ranking Test	<ul style="list-style-type: none"> ▪ Determine if any of the test containers have inherent odors by comparison against a presumed odor-free glass beaker. ▪ If any differences are found, determine which container is different by the least significant difference (LSD) statistical test. 	$H_0: A = B = C = D$
Multiple Comparison Test	<ul style="list-style-type: none"> ▪ Determine if container size affects intensity perception of a known odorous compound by comparison to the 500 mL glass Erlenmeyer flask. ▪ Determine, by statistical analysis, the relative differences in odor intensities of containers found to be significantly different from the Erlenmeyer flask. 	$H_0: R = A, B, \text{ and } C$
FPA Testing	<ul style="list-style-type: none"> ▪ Determine if a larger plastic cup could produce more similar geosmin threshold data to the 500 mL Erlenmeyer flask. ▪ Determine if the type of container holding the reference standards made an impact on odor intensity data. 	H_0 : Erlemeyer geosmin threshold = geosmin threshold of large high-impact polystyrene cup.

TABLE 3.2
Summary of Test Container Characteristics

Container	Total cup volume (mL)	Sample volume added (mL)	Volumetric ratio of air to water	Head space (cm ³)	Typical cost ¹
500mL wide-mouth Erlenmeyer flask	510	200.0	1.55	310.0	\$ 118.67
250mL glass beaker	264	103.5	1.55	160.5	\$ 24.83
Opaque polystyrene plastic cup (red) ²	266	104.3	1.55	161.7	\$ 1.39
Translucent clear K-resin plastic cup ³	207	81.2	1.55	125.8	\$ 1.19
Milky polypropylene plastic specimen cup ⁴	280	109.8	1.55	170.2	\$ 79.33
Translucent clear high-impact polystyrene cup ⁵	500	196.1	1.55	303.9	\$ 1.42

¹ Costs of glassware and specimen cups based on unit price from commercial scientific suppliers. Flasks sold in a case of 6 and beakers sold in a case of 12. Costs of disposable plastic cups based on purchase of 50-100 count packages at local retail stores.

² Opaque polystyrene plastic cups from Solo®, unit price based on a pack of 50 cups.

³ Translucent clear K-resin plastic cups from Kroger®, unit price based on a pack of 50 cups.

⁴ Milky polypropylene plastic specimen cups from Fisher®, unit price based on pack of 100 cups.

⁵ Translucent clear high-impact polystyrene plastic cups from DART®, unit price based on pack of 50 cups.

Ranking Test				
Name:	_____	Date:	_____	
Type of sample:	drinking water			
Characteristic studied:	odor intensity			
Instructions				
1.	Receive the sample tray and note each sample code below according to its position on the tray.			
2.	Swirl and sniff each sample, holding the container by the bottom. Note the intensity of each odor sample. Wait at least 30 seconds between samples.			
3.	Write "1" in the box of the sample which you find has the LEAST INTENSE odor. Write "2" for the next intense, "3" for the next, and "4" for the container with the MOST INTENSE odor.			
Code	_____	_____	_____	_____
Rank	<input style="width: 50px; height: 20px;" type="text"/>	<input style="width: 50px; height: 20px;" type="text"/>	<input style="width: 50px; height: 20px;" type="text"/>	<input style="width: 50px; height: 20px;" type="text"/>

FIGURE 3.1 Sample worksheet for ranking procedure.

Multiple Comparison Test			
Name: _____	Date: _____		
Type of sample: drinking water			
Characteristic studied: odor intensity			
Instructions			
1.	You have 4 samples to compare for odor intensity. You have also been given a reference sample labelled "R".		
2.	Swirl and sniff each sample, holding the container by the bottom. Note whether each sample is more or less intense than the reference. Also note the degree of difference between it and the reference. Wait at least 30 seconds between samples.		
3.	Check the appropriate box for each sample that describes its relationship to the reference and the degree of difference that exists.		
Sample Code:			
	_____	_____	_____
More intense than "R"	_____	_____	_____
Equal to "R"	_____	_____	_____
Less intense than "R"	_____	_____	_____
Degree of Difference:			
None	_____	_____	_____
Slight	_____	_____	_____
Moderate	_____	_____	_____
Much	_____	_____	_____
Extreme	_____	_____	_____

FIGURE 3.2 Sample worksheet for multiple comparison procedure.

TABLE 3.3
Results of Ranking Procedure¹

	250 mL glass beaker	Opaque polystyrene plastic cup	Milky polypropylene plastic specimen cup	Translucent clear K-resin plastic cup
average rank	2.4 ²	2.6 ²	3.4 ³	1.7 ⁴
std dev	1.1	0.9	0.9	1.0

¹ Containers were ranked 1 through 4, with 1 possessing the least odor and 4 the strongest. Results based on the scores of 50 panelists.

² Glass beaker and opaque polystyrene plastic cup were determined not significantly different from one another ($\alpha = 0.05$).

³ Milky polypropylene plastic specimen cup was found to be significantly stronger in odor than the other cups.

⁴ Translucent clear K-resin plastic cup was determined significantly weaker in odor than all other cups.

TABLE 3.4
Results of Multiple Comparison Procedure¹

	250 mL glass beaker	Opaque polystyrene plastic cup	Translucent clear K-resin plastic cup
average score ²	4.12	4.34	3.88
std dev	1.3	1.5	1.3

¹ Panelist responses were converted to a 9-point scale, with 1 indicating an extremely weaker odor intensity compared to the Erlenmeyer flask and 9 indicating an extremely stronger odor intensity. Results based on 50 panelists.

² Results based on a score of 5 being equal in odor intensity to the 500 mL Erlenmeyer flask reference. No test containers were significantly different from the reference Erlenmeyer flask ($\alpha = 0.05$).

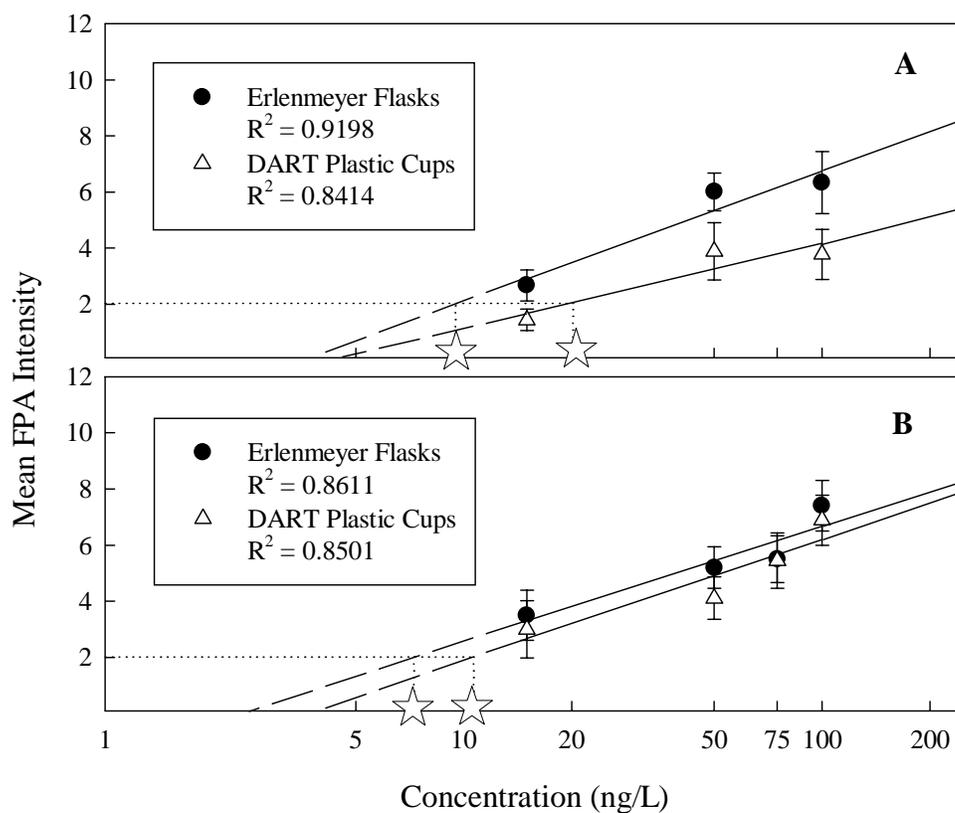


FIGURE 3.3 Comparison Weber-Fechner plots of geosmin using Erlenmeyer flasks and translucent clear high-impact polystyrene plastic cups (DART®). (A) Panelists presented with one set of geosmin reference standards in 500-mL Erlenmeyer flasks and then asked to immediately rate the intensity of geosmin in 3 500-mL Erlenmeyer flasks and 3 500-mL plastic cups. (B) Panelists were presented with a set of geosmin standards in 500-mL Erlenmeyer flasks and asked to rate the intensity of geosmin in 4 unknown samples presented in Erlenmeyer flasks. On the following day panelists were given geosmin reference standards in 500-mL plastic cups and asked to rate the intensity of geosmin in 4 unknown samples presented in plastic cups. Dashed lines represent theoretical extension of Weber-Fechner line beyond those concentrations evaluated by panelists. Stars represent geosmin OTC values at FPA intensity “2”.

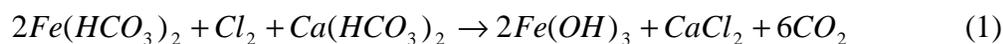
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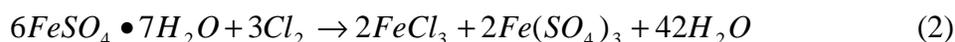
Appendix A. Summary of Other Dechlorinating Agents

Activated carbon. For centuries, activated carbon has been used as a filtration medium for improving water quality. Today, activated carbon exists in two major forms: powdered activated carbon (PAC) and granular activated carbon (GAC). The beverage industry relies heavily upon activated carbon filtration to purify influent water, thus improving their product. Wastewater utilities have used activated carbon to remove harmful chlorine residual before discharge to the environment. The absorption mechanism of activated carbon provides a highly efficient way to remove chlorine, although reaction rates may vary with chlorine concentration, type of residual, carbon particle size, pH, and absorbed organic matter (Snoeyink and Suidan 1975). Unfortunately to this study, the absorption mechanism of activated carbon also removes dissolved organic matter. In drinking water, activated carbon has been used to alleviate taste-and-odor problems. Since activated carbon cannot be used to dechlorinate without simultaneously removing organics, it will not be suitable for this study.

Iron compounds. Iron compounds have long been used as coagulants in the drinking water industry. Iron is also an effective reducing agent, which is known to react with chlorine in certain oxidation/reduction reactions. Ferrous bicarbonate [$\text{Fe}(\text{HCO}_3)_2$] removes free and combined chlorine according to the following equation (White, 1986):

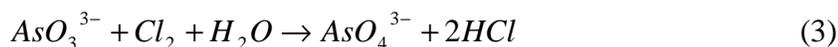


As is shown in the equation, this reaction both consumes alkalinity and releases a significant amount of carbon dioxide gas, thereby raising the pH. Ferrous sulfate (FeSO_4) also reduces chlorine (White 1986):



This reaction also consumes alkalinity and its efficiency is highly pH dependent. Since iron is such a powerful reducing agent, it is likely that both of these compounds will reduce odor-causing compounds as well as remove the unwanted chlorine, making iron compounds unsuitable for this study.

Sodium arsenite. Sodium arsenite is a white or gray odorless powder that has been used as a pesticide, hide preservative, and ingredient in dyeing. Arsenite ion also reduces chlorine according to the following equation (Durrant and Durrant 1970):



Analysis of the above equation shows that 1.73 mg of arsenite ion are needed to reduce 1 mg of chlorine as Cl_2 :

$$\frac{122.9mg \text{ AsO}_3^{3-}}{1mmol \text{ AsO}_3^{3-}} \times \frac{1mmol \text{ AsO}_3^{3-}}{1mmol \text{ Cl}_2} \times \frac{1mmol \text{ Cl}_2}{70.906mg \text{ Cl}_2} = 1.73 \text{ w/w AsO}_3^{3-} \text{ to Cl}_2$$

Arsenite, as a derivative of arsenic, is both a carcinogen and teratogen. The high toxicity of this substance makes it unfit for this project.

Sodium sulfite. One of many sulfurous dechlorinating agents, sodium sulfite has been used in pulp production, bleaching of straw, wool, and silk, photographic developing, and acid washing of jeans (Lind 1995; Merck 1983). Sodium sulfite is a white, odorless powder that reacts with chlorine according to the following equation (Connell 1996):



Unlike other sulfurous dechlorinating agents, sodium sulfite reduces chlorine independent of pH (Lind 1995). Stoichiometric dosing can be determined as follows:

$$\frac{126.037\text{mg } Na_2SO_3}{\text{mmol } Na_2SO_3} \times \frac{1\text{mmol } Na_2SO_3}{1\text{mmol } Cl_2} \times \frac{1\text{mmol } Cl_2}{70.906\text{mg } Cl_2} = 1.78 \text{ w/w } Na_2SO_3 \text{ to } Cl_2$$

As with other sulfur compounds, the production of sulfurous odors is important to this study.

Sodium sulfite begins as an odorless solid but may react to produce odors when in solution.

Other dechlorinating agents. The following table (A.1) summarizes dechlorinating agents not pursued in this study. Reactions and stoichiometry are provided for most agents.

TABLE A.1
Summary of Dechlorinating Agents

Dechlorinating Agent	Reaction/ Approximate Dose	Advantages	Disadvantages	Pursue?
Activated Carbon PAC or GAC form	Adsorption mechanism	<ul style="list-style-type: none"> High rates of chlorine removal 	<ul style="list-style-type: none"> Removes odor compounds 	NO
Ethylene Diamine C ₂ H ₈ N ₂ Liquid			<ul style="list-style-type: none"> Strong ammonia odor 	NO
Ferrous Bicarbonate Fe(HCO ₃) ₂	$2\text{Fe}(\text{HCO}_3)_2 + \text{Cl}_2 + \text{Ca}(\text{HCO}_3)_2 \rightarrow 2\text{Fe}(\text{OH})_3 + \text{CaCl}_2 + 6\text{CO}_2$ 5.02 : 1 dosing	<ul style="list-style-type: none"> Produces a coagulant Intermediate ferric chloride Removes free or combined chlorine 	<ul style="list-style-type: none"> Reacts slowly Releases significant amount CO₂ Most likely reduces odors as well 	NO
Ferrous Sulfate FeSO ₄ Liquid or solid	$6\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3 + 2\text{Fe}_2(\text{SO}_4)_3 + 42\text{H}_2\text{O}$ 7.84 : 1 dosing	<ul style="list-style-type: none"> Forms a coagulant 	<ul style="list-style-type: none"> Highly pH dependent May reduce odors as well 	NO
Formic Acid CH ₂ O ₂ liquid		<ul style="list-style-type: none"> Strong reducing agent 	<ul style="list-style-type: none"> Vinegar odor Caustic to skin 	NO
Hydrogen Sulfide H ₂ S Compressed gas	$\text{H}_2\text{S} + 4\text{Cl}_2 + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 8\text{HCl}$ 0.12 : 1 dosing $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow \text{S} \downarrow + \text{H}_2\text{O}$ 0.48 : 1 dosing	<ul style="list-style-type: none"> Reacts instantaneously 	<ul style="list-style-type: none"> Reaction pH-dependent Smells like rotten eggs Multiple side reactions 	NO
Iodine/Iodate			<ul style="list-style-type: none"> Both smell React with organics 	NO
Manganese	$\text{MnSO}_4 + \text{Cl}_2 + 4\text{NaOH} \rightarrow \text{MnO}_2 + 2\text{NaCl} + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ 2.12 : 1 dosing	<ul style="list-style-type: none"> Doesn't react with chloramines Occurs at pH 7-10 	<ul style="list-style-type: none"> May reduce odors Reaction takes 2-4 hours 	NO
Methane CH ₄ gas	$\text{CH}_4 + 4\text{Cl}_2 \rightarrow \text{CCl}_4 + 4\text{HCl}$ 0.06 : 1 dosing		<ul style="list-style-type: none"> Explosive, fire hazard No reaction between HOCl and CH₄ 	NO
Phenylarsine Oxide C ₆ H ₅ AsO Solution	$\text{C}_6\text{H}_5\text{AsO} + \text{HOCl} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{AsO}(\text{OH})_2 + \text{HCl}$ 3.20 : 1 dosing	<ul style="list-style-type: none"> Easily used Widely available Well known stoichiometry 		POSSIBLE
Sodium Arsenite Na ₃ AsO ₃ White powder form	$\text{Na}_3\text{AsO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_3\text{AsO}_4 + 2\text{HCl}$ 2.70 : 1 dosing	<ul style="list-style-type: none"> Quick reaction Doesn't interfere in GC analyses 	<ul style="list-style-type: none"> Highly toxic to humans Carcinogen 	NO
Sodium Bisulfite NaHSO ₃ White powder	$\text{NaHSO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{NaHSO}_4 + 2\text{HCl}$ 1.47 : 1 dosing	<ul style="list-style-type: none"> Convenient Costs less Easily used 	<ul style="list-style-type: none"> Produces an odor 	NO
Sodium Metabisulfite Na ₂ S ₂ O ₅ Powder form, solution	$\text{Na}_2\text{S}_2\text{O}_5 + 2\text{Cl}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NaHSO}_4 + 4\text{HCl}$ 1.34 : 1 dosing	<ul style="list-style-type: none"> Can be stored for long periods of time if kept cool and dry Lowest addition rate of the sulfur compounds 	<ul style="list-style-type: none"> Masks odor compounds Has an odor of its own 	NO
Sodium Sulfite Na ₂ SO ₃ Liquid form	$\text{Na}_2\text{SO}_3 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ 1.78 : 1 dosing	<ul style="list-style-type: none"> No known odor of its own 	<ul style="list-style-type: none"> Possibility of interaction with odor compounds 	POSSIBLE
Sulfur Dioxide SO ₂ Compressed gas	$\text{SO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{H}_2\text{SO}_4$ 0.90 : 1 dosing	<ul style="list-style-type: none"> Widely available Highly effective Reacts with free and combined chlorine 	<ul style="list-style-type: none"> Pungent odor Expensive to maintain Safety hazards Toxic, corrosive 	NO

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Appendix B. Standard Procedure for Dechlorination of Drinking Water Samples for Odor Analysis

Preparation of Dechlorinating Agents

Hydrogen peroxide may be purchased in a 3% solution from any local grocery or drug store.

Ascorbic acid may be ordered in its solid crystalline form from chemical supply companies such as Fisher Scientific. Ascorbic acid should then be dissolved in ultrapure water (such as Milli-Q or Nanopure) to produce a solution of 5 g/L.

Dechlorination

1. Determine approximate chlorine content of water sample. This can be done by the DPD colorimetric procedure or amperometric titration (Standard Methods 4500-Cl G and 4500-Cl D, respectively).
2. Place 200 mL of water sample into a clean 500-mL Erlenmeyer flask.
3. Dose water sample with appropriate (approximate) amount dechlorinating agent (Table B.1). Dosing does not need to be exact but should be *at least* the amount listed in Table B.1. Overdosing does not seem to affect odor characteristics of water samples.
4. Swirl flask around several times and place in water bath. Perform sensory testing as usual.

TABLE B.1
Dechlorinating Agent Dose Chart

Dechlorinating Agent	Strength of Dechlorinating Agent	Approximate Chlorine Concentration (mg/L as Cl ₂)	Dosage of Dechlorinating Agent
Ascorbic acid	5 g/L	1	1.2 mL
		2	2.4 mL
		3	3.6 mL
		4	4.8 mL
Hydrogen peroxide	3% (drug-store grade)	1	40 µL
		2	80 µL
		3	120 µL
		4	160 µL

VITA

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