TASTE AND ODOR REMOVAL FROM THE INTERNATIONAL PEACE GARDEN WATER USING OXIDATION, COAGULATION, AND CARBON ADSORPTION

BY

MOCHAMMAD NATSIR

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirement
for the Degree of

MASTER OF SCIENCE

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ABSTRACT

In the last few years, the International Peace Garden water treatment plant has experienced taste and odor episodes of a distinct earthy character. These odor problems have been associated with algal blooms in Lake Stormon from which the raw water has been drawn. Copper sulfate, lake aeration, and the existing treatment processes (i.e. permanganate oxidation, alum coagulation, PAC adsorption, and mixed-media filtration) have been found ineffective for controlling the problems.

This study was designed to determine the best available technology for removing the taste-and odor-causing compounds. A series of jar-tests providing a reasonable simulation of the full-scale plant was established to identify the optimum conditions for permangation, alum coagulation, and PAC adsorption. In the subsequent tests, the use of a GAC pilot column as a postfilter-adsorber was studied. An experiment using fresh raw-water was conducted under the optimized conditions to confirm the results from lab-tests. The effectiveness of the treatment processes was evaluated by sensory analysis.

The results demonstrated that permanganate and PAC were ineffective for removing the earthy odor. On the other hand, an alum dose of 150 mg/L removed a considerable portion of the odor. A GAC column with an empty bed contact time of 10 minutes was required to remove the remaining odor. Conclusively, GAC adsorption following the exisiting coagulation process is the best available technology that could be used to remove the taste-and odor-causing compounds from the International Peace Garden water.

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Chapter 1

INTRODUCTION

Taste and odor are generally considered the most primitive senses on the human evolutionary scene. Taste is a very short distance sense operating only on food or drink already in the mouth. Odor, on the other hand, is a remote sense that informs us about the environment and often gives early warning of danger. The belief that early man relied on these senses for survival may, therefore, be accepted.

The primitive senses have adapted to the challenge. Modern man utilizes them to appreciate foods, beverages, and perfumes for enjoyment. The same senses are also extensively involved in water and air pollution control for public health. Lenihan (1974) noted that "Taste and smell, no longer a matter of life and death in unfriendly surroundings, contribute greatly to our health, happiness, and enjoyment of the world around us".

Many different compounds causing taste and odor have been found to have health-related effects. Some substances of this category, such as trichloroethylene (a camporous-smelling substance), cannot be detected by smell at their toxic level (Amoore 1986). However, some others (such as phenols) emit detectable odors at concentrations lower than their specified toxic thresholds (Suffet and Segall 1971). Therefore, odor could be a sensitive indicator of real or potential hazards in the water.

Taste and odor appear to be major properties affecting acceptabillity of drinking water. Since pure water is recognized to be tasteless and odorless, any kind of taste or odor present in drinking water would be undesirable. However, distilled water, that is tasteless, is generally considered to be less pleasant to drink than high-quality waters.

Chemical pretreatment, filtration, and disinfection have successfully been practiced to eliminate public concerns over waterborne diseases. In Western Europe and North America, where the consumers can take safe water for granted, many public complaints of unpleasant tastes and odors in the tap water have been documented. Although the majority of these problems was not due to a hazardous concentration of a contaminant compound, concerns over tastes and odors gave further impetus to the desire to obtain potable and palatable water.

Problems of taste and odor in water supplies can be classified according to their occurance as natural or man-made. Naturally occuring tastes and odors include those caused by microorganisms (notably bacteria and algae) in any part of the systems or by dissolved gases, salts, or base minerals that find their way into the raw water sources. Man-made problems include those caused by industrial chemicals that contaminate the raw water sources, by compounds produced during treatment processes, or by materials that leach from linnings of distribution facilities. Frequently, the distinction is not clearly-cut, as the disposal of contaminants may stimulate the growth of objectionable microorganisms.

Organoleptic (taste and odor) quality of drinking water can optimally be described by sensory analysis (Standard Methods 1989). An individual measurement results in a subjective discription, because of inherent variation in sensitivity to taste and odor. The implementation of sensory panel methods improves the objectiveness of the results. However, maintaning a large expert panel over a long period could be impractical.

Chemical analysis employing sophisticated instruments has been put forth to avoid routine panel measurements. The organoleptic characteristic of a contaminant can only be defined if a relationship between the concentration of this contaminant and its taste or odor intensity has been established by a trained panel. Although individual organoleptic properties of few contaminants have been characterized, most organoleptic problems are too complex to permit their definition by chemical analysis (Standard Methods 1989).

Standard remedies for controlling tastes and odors in water supplies fall into two categories: preventive and corrective measures. Preventive measures are efforts to prevent the development of tastes and odors in supply sources. Common practices of this category are water pollution control in watershed areas, application of algacides, and reservoir aeration. Corrective measures are attemps to remove objectionable tastes and odors from existing supplies. Highly studied methods of this category include aeration, coagulation, oxidation, and activated carbon adsorption.

Perhaps more than any other treatment process, taste and odor control depends heavily on the local circumstances. American Water Works Association Research Foundation and Lyonnaise des Eaux (1987) noted that there are hazards in translating a treatment scheme from work by others. The identified hazards include "...differing stability of water quality (are the tastes stable or do they change with times); different intake and treatment plant characteristics, which may allow different degrees of survival and regrowth of organisms; and different seasonal or upstream watershed characteristics, which may change a condition at the treatment plant". Nevertheless, inadequate guidance from the publised information may lead to an undirected trial and error procedure.

This study is proposed to present selected information from the literature and to evalute the performance of some corrective measures that were applied to the International Peace Garden water. The selective information includes physiology of taste and odor perception, sources of tastes and odors in drinking water, and methods for detecting and controlling taste and odor problems. Since the laboratory study relied on sensory analysis, taste and odor perception is discused in detail in a separate chapter.

The major objective of the laboratory study is to determine the best available technique (BAT) for controlling the occurance of taste and odor compounds in the International Peace Garden water. The performance of alum coagulation, permanganate oxidation, and powdered and granular activated carbon adsorption was evaluated with respect to taste and odor removal in terms of threshold odor number (TON). The first step taken after characterizing the nature of the problems was optimising the existing processes to minimize recomended modifications.

Description of the Case Study

The International Peace Garden is located on the border of North Dakota and Manitoba, with 930 hectares of land spanning the international boundary. In order to provide drinking water in this living monument, a water treatment plant with a production capacity of 200 gpm (12.6 L/s) was constructed in 1981 and located in the United States region. The raw water for this treatment plant is drawn from Lake Stormon in the Turtle mountain region of Manitoba, Canada. As are most lakes in Turtle Mountain, Lake Stormon is a remnant of the glaciers that once covered the area. This lake receives rain and spring run-off from the surrounding area and a small amount of domestic sewage. Since the treatment plant serves both sides with the same water, it must be operated to meet both the American and Canadian drinking water standards.

The treatment plant installed is an Aquarius-AQ40 produced by Neptune-Micro Floc. Essentially, this structure of fabricated steel, consists of two identical compartment trains each of which provides rapid-mixing, flocculation, sedimentation, and filtration (Figure 1.1). Rapid-mixing is done in a rectangular basin with an effective volume of 3.5 m^3, while flocculation is conducted in baffled rectangular basins with a detention time of 17 minutes. The sedimentation basins are equipped with horizontal plate settlers to enhance the removal of the flocculated particles. Finally, mixed-media filters with surface areas of 40 sq ft (3.72 m^2) are provided to remove the unsettled particles at a filtration rate of 5 gpm/sq ft (0.20 $m^3/m^2/min$). This treatment unit allows for the use of certain additional chemicals, such as potassium permanganate and powdered activated carbon.

Originally, the treatment plant was designed to conduct a conventional purification process for removing gross particles and deliberate reduction of pathogenic microorganisms. First of all, the raw water pumped from the lake is hydraulically mixed with 150 mg alum/L and 0.5 mg coagulant-aid/L in the rapid-mix basin. The coagulated water is then introduced to the flocculation basin through a calibrated weir. Next, the flocculated water flows to the sedimentation basin where most of the flocs are settled-out. Just before filtration, a metered quantity of sodium bicarbonate is added to adjust the pH of the clarified water. Finally, the treated water is disinfected using sodium hypochlorite.

In the last few years, the treatment plant has experienced taste and odor episodes of a distinct earthy character. These organoleptic problems have been associated with algal blooms in Lake Stormon from which the raw water has been drawn. Surface applications of copper sulfate, an algicide, has been practised to mitigate the growth of the algae. More recently, two aerator devices have been installed to reduce the occurance of taste and odor in the lake. Nevertheless, these preventive efforts have been considered ineffective.

Two additional chemicals, potassium permanganate and powdered activated carbon, have been applied to reduce the occurrence of the earthy smell in the finished water. One milligram per liter of potassium permanganate has been injected into the transmission pipe. This point of application was chosen to permit 30 minutes contact time. The permanganated raw water has then been delivered to the treatment plant. In order to remove the remaining odorous compounds, 15 mg/L of powdered activated carbon has been fed into the coagulated water. However, this combination has been unable to completely remove the earthy smell.

This objectionable odor remains a major concern of the International Peace Garden water treatment plant. One of the reasons is that the treatment plant has to satisfy the American and Canadian drinking water standards. According to the National Secondary Drinking Water Standard (1979), the maximum contaminant levels in terms of odor is 3 threshold odor numbers (TONs). The Guidelines for Canadian Drinking water Quality (1989) recommended that taste and odor be inoffensive. The other reason is that any kind of unpleasant taste and odor present in the finished water can cause consumers to reject the tap water as unfit, regardless of its bacteriological quality. These concerns led to the demand for a complete study on taste and odor control.

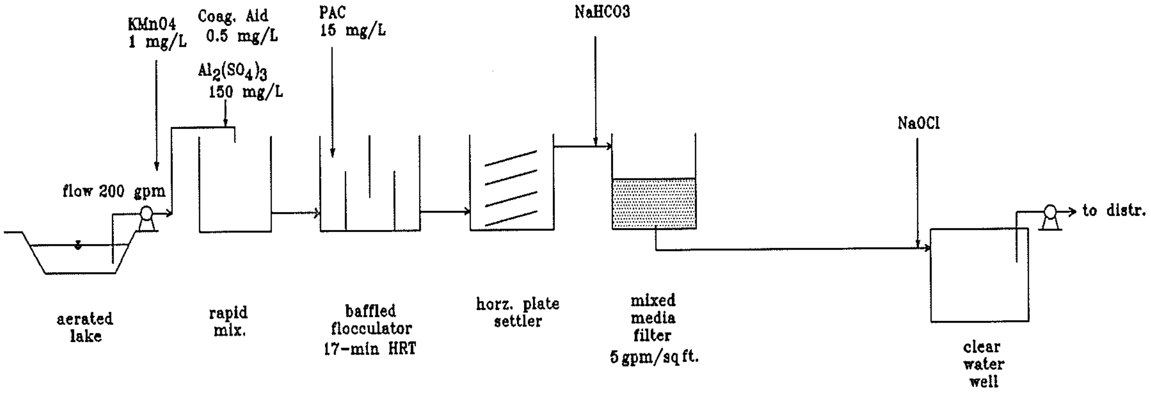


Figure 1.1 Existing Treatment Scheme

Chapter 2

LITERATURE REVIEW ON TASTE AND ODOR PERCEPTION

Organoleptic (taste and odor) sensations result mainly from chemical stimulation of the receptor cells in the mouth and nose. The stimuli are chemical in nature so that taste and odor are often termed as chemical senses. The way in which a stimulant activates the chemoreceptors to produce an impression remains a mystery, even though certain theories may be partially acceptable. This lack of understanding has led the researchers to develop classification systems based on empirical results and intelligent interpretation. An extensive vocabulary expressing feeling sensations has also been introduced to complete the organoleptic description. This adds to the number of sensations between which people are able to differentiate.

2.1 PHYSIOLOGY OF TASTE SENSATION

2.1.1 Receptor Organs

The organs of taste, known collectively as the taste buds, are embedded in the stratified squamous epithelium and are present particulary in the vallate and fungiform papillae. The vallate papillae are so arranged as to form a V-shape that separates the posterior one-third from the anterior two-third of the tongue. The fungiform papillae are mostly spaced on the sides and tip of the tongue and are unevenly distributed over the surface of the tongue. The taste buds are also found on the roof of the mouth, on the epiglottis, in the pharynx and in the throat (Crouch 1972).

Each taste bud consists of a number of supporting cells and some gustatory (receptor) cells. The supporting cells seem to be a packing material, some of them form the wall of the pocket and some others are scattered between the gustatory cells of the bud. The gustatory cells are bipolar, each of which consists of a small amount of cytoplasm and a large nucleus. The peripheral end of a gustatory cell is supplied with a tiny hair which projects into the mouth through the gustatory pore, while the other end is joined to a nerve fibre leading to the brain. By having a very short life (measured only in days), the gustatory cells are found to be a unique part of the nervous system (Crouch 1972 and Lenihan 1974).

2.1.2 Sensation Theories

A number of theories attempting to provide a scientific explanation for the sense of taste have been proposed. Some of them use physical and chemical variabilities of compounds as the starting point. In 1956, Beidler (as cited by E.A. Sigworth 1957) utilized certain electronic instruments to observe the electrical responses of the gustatory cells of many different kinds of animals. According to this experiment, taste sensation involves adsorption and ion-exchange principles. On the other hand, Pfaffman (1964) demonstrated that a taste impression is initiated by a monomolecular reaction of the weak-interaction type associated with hydrogen bonding. Like most theories of taste, these two fit quite well with the experimental evidence, but fail to explain satisfactorily the exact operation of the odorant molecule-receptor cell interaction.

Certain theories rely on response patterns of the receptor cells and their corresponding nerve fibres. In addition to the hydrogen bond interaction, Pfaffman (1964) also reported that only a few of the taste buds appear to have a specialized task, while the others respond to more than one basic stimulus. Lazarev (1970) as cited by Suffet and Segall (1971) and Crouch (1972) were not content to accept this theory and supposed that the taste buds are separately sensitive to sweet, salt, sour, and bitter stimuli. This theory is supported by the evidence of the distribution of taste sensations over the tongue. Based on intelligent observation and interpretation, Suffet and Segall (1971) concluded that taste appears to be an integrated pattern of nerve-impulse response rather than selective receptor stimulation process.

Lenihan's hypothesis about response patterns of the receptor cells nerve interaction may be an exception. Lenihan (1974) determined that the gustatory cells have a very short life, measured only in days. The dead cells will be replaced by new cells. Therefore, Lenihan hypothesized that all the gustatory cells are made to a general-purpose specification and that the specialized response is programmed by instruction delivered from the nerve. At this level of understanding, one may conclude that the taste buds existing in the vallate papillae on the back of the tongue are programmed to respond to bitter sensation, most of those present in the fungiform papillae on the sides and tip of the tongue are programmed to be separately sensitive to sour, salt, and sweet stimuli, and those irregularly spaced on the tongue and other site are programmed to have broad response patterns including feeling sensations.

To be tasted, a substance must be in solution and able to contact the receptor cells. The mouth is provided with glands to ensure proper dilution. By convention, there are only four basic taste sensations, i.e. sweet, bitter, salty, and sour. Recognition of these primary taste factors is to some extent concentrated at certain locations on the anterior two-third of the tongue surface. Sweet tastes are mostly appreciated at the tip of the tongue, while bitter sensations are recognized on the back of the tongue. Salty and sour tastes are detected on the sides of the tongue, which the sour areas are behind the salty areas (Crouch 1972). Accordingly, for a sample to be effectively tasted, it must be dispersed over the tongue surface.

2.1.3 Taste Sensitivity

Threshold taste concentration is the lowest concentration at which a compound can be tasted by an individual. Human sensitivity to taste sensations, differs somewhat among individuals, and even a person will not be consistent in sensitivity over time. Besides normal human variability, age may be the most significant factor that effects the sensitivity to taste. Lenihan (1974) indicated that a baby has more taste buds than an adult, but they are not fully developed functionally and some of them disappear in adolescence. The developed taste buds remain fully effective up to the age of fifty-five after which they begin to deteriorates with advancing age. Furthermore, Lenihan hypothesized that women are not more sensitive to tastes than men. Finally, he stated that the sense of taste will be impaired from the sense of smell by a common cold, but the sense of taste is not influenced.

2.2 PHYSIOLOGY OF ODOR SENSATION

2.2.1 Receptor Organs

Approximately ten square centimetres of yellowish-brown epithelial tissue (in both nostril) constitute the olfactory region in the uppermost recesses of the nasal cavities. This pigmented tissue contains more than ten million receptor cells that are scattered among the supporting cells. The olfactory cells are bipolar, composed of a small amount of cytoplasm and a large nucleus. Each olfactory cell has at its peripheral end a bundle of very fine hairs. The opposite end of the cell passes through the basement membrane and emerges with the others to form bundles of olfactory nerves. Within the submucosa, these bundles form a network of fibres from which about twenty olfactory nerves lead out. As these nerves leave the epithelium, they come into intimate contact with the mitral cells in the glomeruli of the olfactory bulb of the brain. The sense of smell is, therefore, the only sense which is associated with a distinct brain (Crouch 1972 and Cox 1975).

The nasal mucosa is also supplied with certain receptor cells that are sensory endings of the fifth cranial nerve. These receptors respond to some chemicals, such as ammonia and chlorine, by trigeminal reflex to prevent further sniffing of the irritants. Over stimulation of these cells will be interpreted as a painful sensation (Cox 1975).

2.2.2 Sensation Theories

Numerous hypothesises attempting to explain the olfactory mechanism have been put forth, essentially, most of them indicate that odorants are molecular air borne. They may further be grouped according to the odorant-receptor interaction : those that depend upon physical/actual contact phenomenon and those that deal with vibration or wave characteristic of the odorant and receptor. The first group includes the receptor cell puncture theory, the solubility theory, and the stereochemical theory. A unified theory has also been proposed to combine the two groups. A number of the forgoing theories are summarized in the following section.

The receptor cell puncture theory was proposed by J. T. Davies in 1953. According to this theory, odorant particles must be able to penetrate a receptor cell membrane in the olfactory region. A puncture of this membrane results in disruption of a concentration gradient of potassium and sodium, thereby generating a signal registered by the brain as a specific odor (Cox 1975).

Some researchers, such as E. L. Backman 1917, T. H. Durrans 1920, A. Tschirch 1921, and H. Zwaardemaker 1922, are considered to be the contributors to the solubility theory, with perhaps Durrans being the most comprehensive contributor. This theory explains that odorant molecules are lodged and dissolved readily in the watery mucous since they lower the surface tension of water. A certain amount (depends upon the partition coefficient) of the molecules are then passed to the lipid layer. An additional reaction that takes place in this layer generates a measurable change of energy which is interpreted by the brain as an odor. The intensity of the odor is governed by the solubility of the molecules in the lipid tissue (Cox 1975).

The stereochemical theory proposed by J. E. Amoore in 1952 is considered as an extension of the R. W. Moncrieff theory (1951). Amoore postulated that seven characteristic shapes of vacant sites present in the olfactory region are associated with seven basic odor sensations. An oblate depression is associated with a etherial smell, a hemispherical (or dish) shape with a camphoraceous smell, a wedge shaped cavity (or oblate with a recession) with a minty smell, floral shape with a floral smell, and a ring segment shape with a musky smell. Two other basic sensations, i.e. putrid and pangen, are believed to have no size-shape dependence.

Accordingly, all odorant molecules have a specific molecular shape. When a molecule of the right shape drops into one of the vacant sites, an appropriate odor sensation will be evoked. The stereochemical theory was also contributed by J. Timmermans (1954) and L. J. Mullins (1955) (Cox 1975).

The vibrational theory proposed in 1954 by R. H. Wright stems from the observation that color associated with the presence of electrons might absorb energy from a chemical reaction or from neighbouring molecules. Wright suggested, therefore, that an electron in a molecule of olfactory pigment might be promoted to vibrate by the proximity of another molecule which had the appropriate natural frequency of vibration. The resonance produced by the two vibrations will initiate a signal which could be transmitted along the olfactory nerve to the brain. Natural atomic frequencies emitted by molecules to which the nose is sensitive are termed as osmic frequencies.

In 1964, Wright proved Dyson's hypothesis (1939) that osmic frequencies will correspond to infrared adsorption bands, but revised Dyson's wave number range from 1400-3500 to 50-500. Furthermore, the work of Demerdache and Wright (1967) indicates that characteristic vibrations of a molecule are related to the size, shape, and three dimensional orientation of the functional groups and bonds in the molecule. To be perceived, molecules exhibiting osmic frequencies must have sufficient velocity and the right solubility characteristics (Demerdache and Wright 1967 and Cox 1975).

The occurrence of anosmia (smell blindness) or partial anosmia (merosmia) implies that certain specific types of odor receptors probably exist, which concurs with Amoore's hypothesis. However, Cox (1975) pointed out some hurdles for this theory. First, the stereochemical theory is incapable of explaining why enantiomers have different odors. This theory also lacks any elucidation or analogy in nature of a molecule clearing mechanism in the olfactory epithelium. In addition, conditional probability that a minute amount of an odorant can elicit response may exclude the site-filling hypothesis. That molecule shape can play a role in olfaction is unquestionably true, but the stereochemical theory can, at best, be an extension of a unified theory (Cox 1975).

Many objections to the vibrational theory have been recorded, some of those explained by Cox (1975) are summarized below. Like the stereochemical theory, the vibrational theory can not explain why enantiomers have different odors. Furthermore, if adsorption and/or lipid solubility are relevant to olfaction, then olfaction initiated by molecular vibration would be irrelevant. The fact that deuteration of an odorant shifts its far infrared adsorption maxima to lower frequencies without altering the odor would also seem to discredit the vibrational hypothesis. Nevertheless, Cox adopted certain vibrational principles to answer some olfaction problems.

Since rational prediction, interpretation, and explanation dominate the incumbent theories, Cox (1975) assumed that none of these theories is the general theory. Finally, Cox proposed a unified theory of olfaction. However, this theory seems to combine the forgoing theories of olfaction.

2.2.3 Odor Sensitivity

Compared to the sense of taste, the sense of smell is extremely sensitive and able to discriminate among thousands of different odors. For ethylalcohol, one of the few substances which have a taste independent of its smell, the sense of smell was found to be more than 30 times as sensitive as the sense of taste (Lenihan 1974 and Cox 1975). In addition, the average person can perceive between 2000 and 4000 distinctions in odor character, while the tongue recognizes only four different sensations (Lenihan 1974).

Olfactory sensitivity to specific odors varies widely among individuals in a population. Amoore (1986) reported that when a group of 205 normal-healthy people was subjected to a sensitivity test using pyridine, the individual thresholds exhibited an approximately normal or Gaussian distribution with standard deviation ± 1.76 binary steps. The normal odor sensitivity was found to lie between 1/16 to 16 times the mean detection threshold concentration. If certain abnormal and pathological conditions are considered, this range will be expanded.

Table 2.1 Factors affecting the normal smell sensitivities of healthy people

Classification of Subjects*	Factor	Threshold mg pyridine/L water
Average 40-year-old man	1	4.0
Average woman	1	4.0
18-year-old person	0.5	2.0
62-year-old person	2	8.0
Moderate smoker	1	4.0
Smoking during test	4	16
Chewing during test	4	16
Head cold	4	16
Nasal allergy	4	16
Untrained	1.4	5.6
Undirected test	4	16
Misdirected test	26	100
Odor recognation threshold	3	12

Note : * Average 40-year-old people, unless otherwise indicated
Source : Amoore, J. E. (1986).

The effects of aging, gender, and diurnal cycles on the ability to smell have also been reported. In general, the olfactory sensitivity deteriorates with advancing age.

Amoore (1986) cited that the sensitivity is reduced by half for every 22 years of age after age 20 years. Furthermore, Amoore stated that men are not less sensitive than women with the same age category, although there are contradictory results (Cox 1975 and Bartels et al. 1986). Amoore also reported that moderate smokers are not less sensitive than nonsmokers, provided they have not smoked during the 15 min before the test. Table 2.1 cites the data reported by Amoore (1986).

2.3 AROMA AND FLAVOR

Aroma refers to all sensations perceived by the nose while sniffing. Besides olfactory sensations, there are also feeling sensations due to chemical and physical stimulation of the trigeminal nerves. Feeling sensations include characteristics like pungency (as is experienced while smelling a strong chlorine or ammonia solution) and burning sensation. In this report, aroma is used interchangeably with odor, particularly in the discussion of the flavor profile analysis.

Flavor stands for all taste-and-odor sensations experienced while eating food and drinking baverages. In addition to the chemical stimulation of the taste buds, flavor includes stimulation of the olfactory and trigeminal organs in the nose and the sensory organs in the mouth and throat. Stimulation of these sensory organs is also described as feeling sensations, such as astringency from alum and cooling from menthol. In this report, flavor is used interchangeably with taste and odor, particularly in the discussion of the flavor profile analysis.

2.4 ODOR CLASSIFICATION

The sense of smell is often difficult to articulate. One of the reasons is that the nose has a remarkable ability to distinguish odor sensations. Few odors are pure, but the others are complex mixtures of several separate odors in varying intensity. Lack of standardization will make meaningful compilation of qualitative expressions look like a lexicon of grammatical adjective, for example : unpleasant, putrid, sharp, burning, etc.. Obviously, it is necessary to apply a scheme of odor description that will have the same meaning and significant to everyone.

2.4.1 General Odor Classification

In general, the proposed classification systems have been influenced by the profession of the developers. Amoore (1986) summarized a number of the systems that have traditionally been derived from perfumery and food flavors (on the left-hand side of Table 2.2). The descriptive odor classes presented in the same horizontal line have been considered to be exactly or nearly equivalent. Apparently, there are only 43 reasonable descriptive odors.

The following are some important comments pointed out by Cox (1975) on the particular classification systems.

* Zwaardemaker's classification (1895) may be categorized as chromatoid (primary) and subjective/empirical. This system attempted a comprehensive approach and was found to some extent on experimentation.

* Henning's classification (1915) may be categorized as chromatoid and subjective. This classification is principally a perfumer's system. Although it expresses clearly certain definite categories of odor by the use of descriptive class headings, it failed to provide a means of quantification for simple expression.

* Crocker and Henderson's arrangement (1927) may be categorized as chromatoid and subjective, however it mixed class headings with sub-classes and factors. Any particular odor may be composed of more than one of so called classes in different proportions. A numerical scale of 0 to 8 is usually used to express the occurrence intensity of the particular class heading. In general, this arrangement is considered to be over-simplification.

* Amoore's primary odors (1952) are associated with seven odor receptor sites. This chromatoid arrangement is descriptive of both class headings and factors based on chemical configuration and odor constant. Nevertheless, it is a highly specific classification.

* Harper, Bate-Smith, Land's classification (1968) is a practical description of odor character in which the intensity is expressed on a scale of 0 to 5. This system provides many possible terms so that it has been proven to be serviceable, particulary in sensory panels.

2.4.2 Amoore's Primary Odors (1986)

Amoore (1986) hypothesis that the sense of smell, similar to taste, depends on a number of discrete primary odors. This means that a tremendous number of distinctive odors can be obtained from combinations of the individual odors. Many people are incapable of smelling certain specific odors as others have a blindness for certain primary colors. Obviously, the occurrence of smell blindness or specific anosmia appears to be potentially useful for determination of primary odors. However, this formulation is not as easy as the determination of the four primary tastes.

As cited by Amoore (1986), Marcel Guillot in 1948 stated that people with a specific anosmia (or strictly speaking, hyposmia) lacked the specialzed nervous receptors (nerves, olfactory cells, or molecular receptor sites) for recognizing one of the primary odors. A number of researches, as summarized by Cox (1975), established that hyposmia (decreased odor intensity perception) is a genetic abnormality. Furthermore, Cox pointed out that some illness (including brain lesions, injured olfactory nerves, and obstructed nasal passages) can cause a person to be partially anosmic to a certain odor.

Amoore (1986) concluded that eighty-nine chemicals, which are summarized on the right hand side of Table 2.2, exhibit specific anosmia. Since there is much redundancy among them, Amoore estimated that the number of primary odors is not more than 34. Of these, eight specific odors have been submitted to a detailed study as described below.

Table 2.2 Classification of odors (left hand side)

General Odor Classifications								
Zwaardemaker (1895) 30 (sub)classes	**Linnaeus (1756) 7 classes**	**Henning (1915) 6 classes**	**Crocker & Henderson (1927) 4 classes**	**Amoore (1952) 7 classes**	**Schutz (1964) 9 classes**	**Wright & Michels (1964) 8 classes**	**Harper et al (1968) 44 classes**	**Miscellaneous**
Fruity						Hexyl acetate	Fruity	
Waxy							Soapy	
Ethereal				Ethereal	Etherish		Etherish; solvent	
Camphor				Camphor			Camphor; mothballs	
Clove	Aromatic						Aromatic	
Cinnamon		Spicy				Spice	Spicy	
Aniseed						Benzothiazole		
Minty				Minty			Minty	
Thyme								
Rosy								
Citrous		Fruity				Citral	Citrous	
Almond					Spicy		Almond	
Jasmine		Flowery		Floral			Floral	
Orange blossom	Fragrant		Fragrant		Fragrant		Fragrant	
Lily								
Violet								
Vanilla					Sweet		Vanilla; sweet	
Amber								
Musky	Ambrosial			Musky			Musk	
Leek	Alliaceous						Garlic	
Fishy							Ammonia; fishy	
Bromine								
Burnt		Burnt	Burnt		Burnt	Affective	Burnt	
Phenolic							Carbolic	
Caproic	Hircine		Caprylic				Sweaty	
Cat urine								
Narcotic	Repulsive							
Bed bug							Grassy	
Carrion	Nauseous						Sickly	
Fecal							Fecal; animal	
		Resinous				Resinous	Resinous; paint	
		Foul		Putrid	Sulfurous	Unpleasant	Putrid; sulfurous	
			Acid				Acid	
					Oily		Oily	
					Rancid		Rancid	
					Metallic		Metallic	
							Meaty	
							Moldy	
							Bloody	
							Cooked vegetable	
								Cyanide
								Malty
								Sulfide
				Pungent*		Trigeminal*	Pungent; and five others*	

Note : * Nonolfactory
Source : Amoore (1986)

Table 2.2 Classification of odors (right hand side)

Specific Anosmia Analyses					
Reputed Specific Anosmias				**Established Primary Odorant**	**Probable Primary Odor**
γ-Undecalactone	Isoamyl acetate				
Ethylene dichloride	Trichloroethylene	Benzene	Ketones (3)		
1,8-Cineole	Naphthalene	*p*-Dichlorobenzene	Adamantane	1,8-Cineole	Camphor
Eugenol	Benzyl alcohol	Anisole			
Cinnamaldehyde	Salicylaldehyde				
Menthone	Menthol	*tert*-Butyl carbinol	Carvone	*l*-Carvone	Minty
Thymol					
Geraniol	Phenyl ethanol				
Geranial					
PEME carbinol					
Lyral					
Ionone	Farnesol				
Benzaldehydes (3)	Benzyl salicylate	Cyclotene			
Cedryl acetate	Thujamber				
Macrocyclic musks (4)	Nitro musks (2)	Versalide		ω-Pentadecalactone	Musky
Allyl isothiocyanate	Phenyl isothiocyanate	Allicin	Propenyl sulfenic acid		
Hexylamine	Trimethylamine	*N*-Methyl pyrrolidine		Trimethylamine	Fishy
Iodoform					
Pyridine					
p-Ethyl phenol	4-Chloro aniline				
Aliphatic acids (3)	Phenylacetic acid			Isovaleric acid	Sweaty
Steroid ketones (3)	Androstenol	Isomorphic ketones (2)		Androst-16-en-3-one	Urinous
Phenyl isocyanide					
Putrescine	1-Pyrroline			1-Pyrroline	Spermous
Skatole	Indole				
Isoamyl alcohol					
Mercaptans (3)	Dimethyl disulfide	Thiophane	Dibutyl sulfide		
Formic acid	Acetic acid				
Diacetyl	Acrylonitrile	3-Buten-2-one			
2-Heptanone	2,4,5-Thiazole	2,3-Pyrazine			
Methional					
Hydrogen cyanide					
Isobutyraldehyde				Isobutyraldehyde	Malty
Hydrogen sulfide					
Formaldehyde*					

Note : * Nonolfactory

Source : Amoore (1986)

If a sufficiently large group of healthy people are tested with a compound to which a number of the members are anosmic, the distribution of their thresholds is bimodal. Bimodality of the distribution, i.e. the average threshold deficit of persons specifically anosmic to the odorant, is more pronounced for compounds closer to the ideal primary odor compound. This primary odorant typically has the lowest odor threshold among the whole family of compounds with similar odor (Amoore 1986).

Eight compounds showing the greatest bimodality (or anosmic defect) in their own classes have been connected to the most descriptive primary odors (Table 2.3) (Amoore 1986). The threshold concentration of the odorants in water are related to the threshold concentration in air by the air-water partition coefficients. Nevertheless, these values may be altered by any form of energy variation, i.e. chemical, light, and heat.

Table 2.3 Olfactometric properties of eight of the primary odorants

		Normal Threshold		**Anosmic Occurrence** *percent*	**Anosmic Defect** *factor*
Primary Odorant	**Primary Odor**	**In Air** *μL/L (v/v)*	**In Water** *mg/L (w/v)*		
Isovaleric acid	Sweaty	0.0010	0.12	3	42
1-Pyrroline	Spermous	0.0018	0.020	16	39
Trimethylamine	Fishy	0.0010	0.00047	6	830
Isobutyraldehyde	Malty	0.0050	0.0018	36	340
5α-Androst-16-en-3-one	Urinous	0.00019	0.00018	47	770
ω-Pentadecalactone	Musky	0.018	0.0018	12	13
l-Carvone	Minty	0.0056	0.041	8	13
1,8-Cineole	Camphorous	0.011	0.020	33	56

Source : Amoore (1986)

2.5 ODOR CHARACTERISTICS

2.5.1 Odorant Properties

To be detected, an odorous substance must be in the vapour state. Cox (1975) hypothesized that substances with high vapour pressures are potentially odorous. The number of molecules that can be given-off is governed by the vapour pressure. Therefore, substances with a higher vapour pressure have greater likelihood of odorous perception. For example, vanilla with a vapour pressure of 214.5 at 100 mm Hg is an odorous substance, on the other hand, carbon dioxide with a vapour pressure of - 100.2 at 100 mm Hg is non-odorous substance. This example also indicates that some substances, although in a vapour form, do not elicit a smell (Cox 1975).

Many materials are able to adsorb certain odorants. The degree of adsorption and tenacity will generally be determined by the surface coarseness, porosity, composition, and color of the adsorbent. Types of adsorption include physical adsorption due to Van der Wall's forces attraction, chemisorption due to sharing of electrons, condensorption due to condensation of the adsorbates onto the adsorbent, and chromosorption due to the color of the adsorbent (Cox 1975).

Furthermore, Cox (1975) summarized that adsorption increases with the molecular weight of the adsorbates, but substances with strong adhering properties to a surface usually have weak odors. In addition, propensity for adsorption normally increases with the darkness of adsorbents. In other words, materials with black color (such as activated carbon) being the most adsorbent. Other materials, such as iron dioxide and aluminum silicate, are also known as adsorbents.

Odor intensity of some odorants can be altered by exposure to ultraviolet radiation. Cox (1975) found that the odor intensity of valeric acid, trimetrhylamine, skatole, and vanilla were reduced by half when they were exposed to ultraviolet wave length for 10, 30, 50, and 120 seconds respectively. This reduction occurred as a result of the formation of ozone during the passage of ultraviolet rays through the atmosphere. Accordingly, Cox concluded that some odorants are destructively reduced by contact oxidation.

2.5.2 Complexities of Odor Perception

The mixing of odorants, that are chemically unrelated, may induce combination effects or masking effects. The simplest combination effect occurs when the resultant odor is more intense with characteristics of the individual components. A combination of two (or more) odorants may also give a third description that is entirely different from the original descriptions (Pengkala 1974 and Bartels et al. 1986).

If this is the case, binary mixtures of thirty-four primary odors at equal concentrations could theoretically give 34x34 new descriptive odors. The number increases exponentially with mixtures of higher order and different concentrations. On the other hand, a strong odor prevents a faint odor from being perceived at the same time. This masking effect is commonly applied to block out a faint objectionable odor by the use of a pleasant odor in a high concentration (Pengkala 1974 and Bartels et al. 1986).

Furthermore, the effects of mixing odorants on odor perception can be categorized as independence, addition, antagonism, and synergism. Independent effect occurs when the resulting odor is the highest of any of its components. Odor addition occurs when the resulting odor is the sum of the individual contributions. Antagonistic effect occurs when the resulting odor is less than expected by direct addition. Synergistic effect occurs when the resulting odor is greater than expected by direct addition (Rosen et al. 1962 and Baker 1963). The data from limited cases of some organic compounds indicated that odor addition and synergism are often the characteristics of the mixtures (Rosen et al. 1962, Baker 1963, and Rosen et al. 1963). These evidences may preclude the use of single-threshold values as criteria for acceptable water.

Chapter 3

LITERATURE REVIEW ON
IDENTIFICATION AND TREATMENT OF TASTES AND ODORS
IN DRINKING WATER

The active fields of research on taste and odor in water supplies can be grouped into three branches : nature of taste-and odor-causing compounds, analytical methods for detecting them and treatment techniques for controlling their occurrences. The development of extremely sensitive techniques and instruments for isolating and identifying compounds that cause tastes and odors in drinking water has improved the understanding of their nature. This improvement has helped the researchers to find better techniques to remove these compounds. The adoption of the flavor profile analysis (FPA), a sensory panel method, has also added a new dimension to the water purification field.

3.1. NATURE OF TASTE-AND ODOR-CAUSING COMPOUNDS

The cause of taste and odor problems in drinking water can be inorganic matter, although most of the problems are due to organic compounds. Bruvold et al. (1969) found that waters with a total dissolved solids content (TDS) less than 1200 mg/l were classified as neutral or taste good by the consumer panel. Furthermore, the researchers determined that water with a TDS of 320-658 mg/L was good, 659-996 mg/L was fair, and 997-1332 mg/L was poor. The secondary contaminant level published by US Environmental Protection Agency in 1984 and Canadian Guidelines for Drinking Water Quality (1989) specify that TDS level be less than 500 mg/L.

The presence of salts or particular metals at a concentration greater than their specified threshold taste will impair the water taste. Based on data obtained from taste assessments, Zoeteman (1978) as cited by American Water Works Association Research Foundation and Lyonnaise de Eaux (**AWWARF and LdE** 1987) recommended maximum acceptable levels of individual salts to prevent an offensive taste, as shown in Table 3.1. Water Research Center (1981) as cited by the same publisher specified that iron, copper, manganese and zinc can be tasted in distilled water at 0.05 mg/L, 2.5 mg/L, 3.5 mg/L and 5 mg/L respectively. In fact, water contains a mixture of inorganic constituents that may show synergistic or antagonistic affects.

In many instances, taste and odor problems are caused by dissolved inorganic gases. A rotten-egg odor of hydrogen sulfide is a common example in supplies fed by groundwater or water from deep reservoirs. The practice of disinfection (halogen and ozone) can also generate offensive odors. At a high residual level, chlorine it self can be objectionable.

Taste-and odor-causing compounds reach the consumers from many different origins. They can be present in the raw-water sources, initiated during treatment process, or introduced into the distribution systems. A taste and odor survey conducted by Sigworth (1957) indicated that most of the troublesome compounds are present in the supply-sources.

Table 3.1 Maximum acceptable levels of salts in water to prevent offensive taste

Constituent	Salt Concentration mg/L	Cation Concentration mg/L
$NaCl$	465	185
$MgCl_2$	47	12
$CaCl_2$	350	105
$NaHCO_3$	630	175
$Mg(HCO_3)_2$(I)*	58	10
$Mg(HCO_3)_2$(II)*	740	120
$Ca(HCO_3)_2$	610	150
Na_2SO_4	-	-
$MgSO_4$	840	170
$CaSO_4$	1020	300

Note : * The taste concentration curve (taste rating versus concentration) for $Mg(HCO_3)_2$ twice trespasses the scale value corresponding to "it has an offensive taste". Therefore, two concentration are presented.
Source : Zoeteman, B. C. J. (1980)

3.1.1 Biological Sources of Taste and Odor in Water

Algae and actinomycetes have long been associated with taste and odor problems in water. Algae were, for the first time, reported as the troublemakers in the third AWWA annual meeting held in 1883 (Wolman 1956). A few years later, Rullman (1895) as cited by Silvey et al. (1950) reported that a culture of actinomycetes produced a pungent earthy odor. From those times, most of taste and odor problems have been attributed to algae and actinomycetes,although protozoans, fungi, and other aquatic biota have been implicated.

Until the 1960s, research on taste and odor appeared to be focused on the microbiological aspects. The intensity of taste and odor episodes was linked with the population density of the organism believed to be the cause of the problems. In fact, intimate relationships between the growth of algae and actinomycetes were observed (Silvey et al. 1950, Silvey and Roach 1964, Silvey 1966). As a result, the actual causes were often debated in the literature.

Based on questionnaire responses received from 241 water utilities in the United States, Sigworth (1957) summarized that the most frequent cause of taste and odor problems was algae (82%) and the next was decaying vegetation (67%). The odors under the classification of decaying vegetation originated from : decaying plants; flushing of stagnant areas and farm land ; and bottom deposits of water bodies. The most prevalent description of these odors was musty and the next was earthy. Both of them are usually used to describe odors caused by compounds that are produced by algae and actinomycetes. Therefore, Sigworth (1957) postulated that many of the problems might be attributed to actinomycetes.

Since the mid-1960s, the emphasis in the taste and odor literature has shifted to the chemical aspects to confirm the nature of the problems. This confirmation relies on isolation techniques and the use of analytical methods, such as gas chromatography-mass spectrophotometry (GC-MS). Recently, a closed-loop stripping analysis (CLSA), which allows identification of organic compounds at low nanogram-per-litre levels, is widely used to detect odor problems in water supplies.

Gerber and Lachevalier (1965) isolated a specific compound having an earthy odor from the metabolic product of Streptomyces (a genus of Actinomycetes). They named this compound "geosmin" from the Greek words "ge" meaning earth and "osme" meaning odor. Gerber (1967) characterized that geosmin is a colorless oil which darkens very slightly on long storage even at 5^0C. in a sealed tube. She also described that geosmin with an indicated molecular formula of $C_{12}H_{22}O$ was not stable to acid but was transformed readily to argosmin which is an odorless and colorless oil with a molecular formula of $C_{12}H_{20}$. Furthermore, she estimated that the boiling point of geosmin is 270^0C. The specified threshold odor concentration of geosmin is 10 ng/L (McGuire et al. 1981).

Medsker et al. (1969) reported that a similar compound to geosmin was isolated from three species of Streptomyces. They named this compound 2-exo-hydroxy-2-methylbornane and identified that its empirical formula is $C_{11}H_{20}O$. Gerber (1969) referred this compound to 2-methylisoborneol (MIB), which is frequently used in the literature. At a dilute concentration, MIB emits an earthy odor, but at a higher concentration MIB produces a musty smell. The specified threshold odor concentration of MIB is 29 ng/L. The formulas and properties of geosmin, MIB, and three other earthy-musty smelling substances illustrated in Figure 3.1 are taken from data assembled by Lalezary et al. (1986).

Geosmin and MIB have also been isolated from blue-green algae. Safferman et al. (1967) isolated an earthy-smelling organic, identified as geosmin from a stock culture of the blue-green alga Symploca muscorum. One year later, Medsker et al. (1968) isolated an identical substance from the Oscillatoria tunis. Tabachek and Yurkowski (1976) recovered MIB from the blue-green alga Lyngbya taken from a fish-farming lake in Manitoba. After these major discoveries, the isolation of geosmin and MIB from blue-green algae quickly followed.

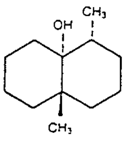
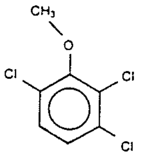
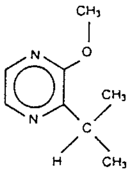
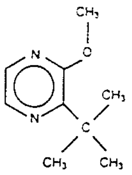
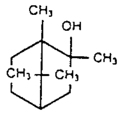
Molecular structure					
Symbol	Geosmin	TCA	IPMP	IBMP	MIB
Molecular weight	182	212	152	166	168
Molecular formula	$C_{12}H_{22}O$	$C_7H_5OCl_3$	$C_8H_{12}ON_2$	$C_9H_{14}ON_2$	$C_{11}H_{20}O$
Name	*trans*-1,10-dimethyl-*trans*-9 decalol	2,3,6-trichloro-anisole	2-isopropyl-3-methoxy pyrazine	2-isobutyl-3-methoxy pyrazine	2-methyl-isoborneol

Figure 3.1 Molecular characteristics and olfactory description of five earthy-musty odorants (Source : Lalezary et al. 1986).

Actinomycetes and Odor Production

The Actinomycetes are aerobic, gram-positive, filamentous bacteria. They closely resemble fungi in overall morphology (Prescott et al. 1990). Several authors define actinomycetes as microorganisms that occupy a distinct position between bacteria and fungi (Silvey et al. 1950, Romano and Safferman 1963). Actinomycetes can degrade an enormous number and variety of organic compounds and play a significant role in the mineralization of organic matter (Prescott et al. 1990).

Actinomycetes are primarily soil inhabitants (Prescott et al. 1990). They are present largely in muds (Silvey et al. 1950) and littoral areas of the shorelines. They play a major role in decomposition of older plant materials, soil humus, and animal materials. In addition, some numbers of this group, particulary of these genus Streptomyces, produce odor-causing compounds such as geosmin and MIB.

Actimomycetes are also found in water, mostly in quiescent rivers and lakes. This aquatic group grows best in water 6-11 in. deep and least readily in lakes of 40 ft. or more in depth (Silvey et al. 1950). Furthermore he noted that actinomycetes grow in quantities in alkaline water. In fact, aquatic actinomycetes appear to mainly originate in run off from the surrounding areas (Silvey et al. 1950, Ramano and Safferman 1963, and Morris et al. 1963).

Certain actinomycetes live within or on algae and higher aquatic plants. Silvey and Roach (1953) observed actinomycetes inside the cells of Cladophora, a green alga. Actinomycetes have been found within numerous algae, including chlorella, anabaena, and Aphanizomanon (Silvey 1953). Silvey (1966) described that actinomycetes have been observed to begin rapid reproduction after blue-green algae had completed their growth. Silvey et al (1950) concluded that Streptomyces may destroy algae, and both aquatic and terrestrial vegetation.

Silvey (1966) described two stages of the actinomycete's life cycle. The primary stage is facultative anaerobic during which the actinomycete remains in an active physiologic state, but it is incapable of producing taste and odorous compounds. When oxygen become available, the actinomycete begins its secondary stage. An aerobic period of 6-18 days will be adequate for the actinomycete to produce detectable odor. However, Prescott et al. (1990) noted that numbers of genus Streptomyces are strict aerobes. In the water industry, interest in the actinomycetes stems from the fact that taste and odor causing compounds are produced during the aerobic stage.

Many actinomycetes have been identified as geosmin and MIB producers. Most of them belong to the genus Streptomyces and few others belong to the genera Nocardia, Actinomyces , and Microbispora. Table A.1 in Appendix A presents data adopted by AWWARF and LdE (1987).

Algae and Odor Production

The most common algae associated with taste and odor problems in water supplies are blue-green algae, green algae, diatoms, and flagellated algae. They may be unicellular, exist as colonies of many shapes, or form filaments. Unlike the others, the blue-green algae are true procaryotic bacteria. They appear blue-green because of blue pigment phycocyanin and chlorophyll. Their photosynthetic system closely resembles that of eucaryotes (Prescott et al 1990). Therefore, recent literature refers to them as Cyanobacteria and taste-and-odor literature places them among the true eucaryotic algae.

Algae commonly exist in water (fresh, marine, brackish) in which they may be suspended (planktonic) or attached on the bottom (benthic). Some algae grow on moist rocks, soil, woods, and trees. Some others live as endosymbiants in various protozoa, mollusks, worms, corals and within plants. Some algae associate with fungi to form lichens (Prescott et al. 1990). In fact, many algae that cause taste and odor problems in water supplies are present in littoral areas of shorelines. This is one of the reasons that the population density of algae is often difficult to correlate with the taste and odor intensity.

Several factors affect the types and activities of algae in surface water bodies. Natural conditions such as topography, soil type, temperature, and hydrogeological cycle significantly determine the characteristics of the algae (Valcik 1975). Sunlight as well as nutrients are also necessary for algal metabolism. Nutrients can enter a water body in a number of ways, which are mostly beyond man's control. However, poor agricultural practices and municipal waste disposal will provide a profound stimulation upon the growth of algae.

Algae can cause tastes and odors in two ways. Many metabolic products of algae are taste and odor - causing compounds. A fraction of these compounds is released during their active existence, while the remainder is kept within the cells until it is liberated at the time the algae die and decompose (Maloney 1963). In addition, the dead cells may serve as a source of nutrition for bacteria, such as the actinomycetes, which produce odorous compounds (Silvey and Roach 1953, Jenkins et al. 1967).

The occurrence of taste and odors have often been associated with the presence of specific algae. Palmer (1962) cited the following relationships. The aromatic odors, which include odors characteristic of vegetables, spices,and garlic, are produced by some diatoms and flagellates. When these organisms are present in larger numbers, fishy (rather than aromatic) odors are generally produced. The grassy odors are typically produced by green algae when they are present in large numbers, although blue-green algae, diatoms, and flagellates may be reported. The musty or potato-bin, earthy or moldy, and septic odors are commonly produced by blue-green algae. Other odors are postulated to be combinations of the grassy and musty odors. The information in Table A.2 in Appendix A is taken from data adapted by AWWARF and LdE (1987).

Blue-green algae, notably Anabaena and Oscillatoria, have been considered to be the major algal producers of geosmin and MIB. The species that have been identified as geosmin and MIB producers are shown in Table A.3 in Appendix A. Interestingly, Microcystis or Anacystis, that has often been implicated as the causative organism of earthy-musty odor episodes, has never been found to produce geosmin or MIB.

Taste and Odor Production by Other Microorganisms

Some bacteria, other than mentioned previously, can generate tastes and odors in water. Ferro-bacteria, which typically grow in deep water and water-distribution systems, can cause unpleasant taste and odors by oxidizing ferrous iron to ferric iron (MacKenthun and Keup 1970). Lin (1976) reported the sulfate-reducing bacteria, particulary Desulfovibria desulfuricans, can reduce sulfates to hydrogen sulfide (a rotten-egg-smelling compound). Jenkins et al. (1967) identified putrid-smelling compounds, mercaptans and dimethylpolysulfides, from the bacterial decomposition of the blue-green algae Microcystis, Oscillatoria, and Anabaena.

Other microorganisms,such as fungi, zooplankton, nematodes, and amoeba, can be other biological causes of tastes and odors in water. Wood et al. (1983) as cited by AWWARF and LdE (1987) stated that some fungi can cause earthy odors in water. When present in large numbers, zooplankton (e.g. the crustaceans Cyclops and rotifer Keratella) can generate fishy odors (Lin 1976a and Lin 1976b). Chang et al. (1960) isolated an oily compound that emits an earthy-musty odor from nematode cultures. They also found that some amoeba are capable of generating taste and odors.

3.1.2 Anthropogenic Sources of Tastes and Odors

Wolman (1956), in his report on 75 years of water quality improvement, stated that World War I resulted in a tremendous expansion of industrial chemicals wasted into water bodies. Furthermore, Wolman noted that the advent of the automobile gave rise to construction of macadam - roads, which are known as sources of phenols and related compounds. These facts resulted in additional problems of taste and odor.

Water-utility personal in the United-States surveyed by Sigworth (1957) listed trade wastes (38%) as the third major source (after algae and decaying vegetation) of tastes and odors in their systems. Phenol was reported as the most frequent cause of this category, with chemical and petroleum oil or oil refinery wastes were the second and third causes respectively. According to this survey, trade wastes often gave rise to extremely high odor concentrations.

Anthropogenic origins of tastes and odors include dispersed chronic pollution in urban areas, municipal and industrial wastewater effluents, and many other sources (AWWARF and LdE 1987). Numerous halogenated organics, such as dichlorobenzene, trichloroethylene, tetrachloroethylene, carbon tetrachloride, and methylene chloride, are widely used as solvents, metal degreasers, cleaning and heat transfer agents, etc. Some of them have been found in many water supplies in the United States (Tate and Arnold 1990). They tend to contaminate drinking water because of their huge production, highly delocalized use patterns, chemical and biological stability, volatility, and negligible adsorption in soils and sediments (AWWARF and LdE 1987). In addition, some of them can be formed during chlorination. Table 3.2 summarizes data adapted from and Tate and Arnold (1990).

Gasoline and its components, such as benzenes, toluene, xylenes, and several alkylbenzenes, are other organic pollutants. These compounds are also used as solvents and components of synthetic organic chemicals. Some of them have been identified in many water supplies in the United States (Tate and Arnold 1990). Their occurrences in drinking water are becoming more frequent, because they are enriched in lead-free gasoline and tend to move faster than other organics (AWWARF and LdE 1987).

Many taste and odor causing compounds in drinking water are constituents of wasterwater effluents, agricultural runoff, and urban runoff that had found their way into the supply sources. Specific compounds identified in municipal wastewater effluents include carboxylic acids, alcohols, phenols, aromatic hydrocarbons, and chlorinated solvents (Garrison et al. 1976). The nature of compounds present in industrial wastewater effluents depends on the type of industry. Some herbicides such as triazines (earthy musty compounds) are frequently found in surface water, because they are highly mobile in water (AWWARF and LdE 1987).

Table 3.2 Odor threshold, toxic level, and application of some halogenated organics

Solvent	Threshold Odor mg/L	Toxic Level mg/L	Application
1,4-Dichlorobenzene	0.0003	0.075	used as solvent in the production of organic chemicals, pesticides, and dyes.
Trichloroethylene	0.5	0.005	used in metal degreasing, dry cleanings, organic synthesis, refrigraments, and fumigants.
Tetrachloroethylene	0.3	0.005	used as a solvent in the manufacture of fluorocarbons and as a heat transfer agent, also form duringchlorination.
Carbon tetrachloride	0.2	0.005	used in the manufacture of chlorofluoromethene, grain fumigants, fire extinguishers, solvents, and cleaning agents.
Methyl chloride		0.005	used in the manufacture of paint removers, insecticides, solvents, cleaners, pressurized spray products, and fire extinguishers, also form during chlorination.

Source : Tate and Arnold (1990).

It is almost impossible to obtain an exhaustive list of organic pollutants that cause tastes and odors in water. However, the list of compounds that has been published by several authors may give a general idea of specific organic pollutants. Baker (1963) published a list of threshold odor levels for 32 organic chemicals (Table A.4 in Appendix A). Van Gemert and Nettenbreijer (1977) published a more comprehensive list and indicated some industries that utilize these compounds (Table A.5 in Appendix A).

3.1.3 Tastes and Odors Generated During Water Treatment

Certain process of water purification (e.g., sedimentation, slow sand filtration, and GAC adsorption) may provide a favourable environment for biological activity to occur. Under certain conditions, the organisms mentioned previously are able to grow and degrade the organic compounds present in the water. Some by-products released in this activity could be taste and odor causing compound, such as phenols, aldehydes, and alkylbenzenes (AWWARF and LdE 1987).

One of the problems associated with chlorination practices is that free chlorine and chloramine residuals can impart objectionable flavors in the water. In general, the identified flavor threshold of chlorine at neutral pH is about 0.2 mg/L. Monochloramine and dichloramine, which are used as alternative disinfectants or are formed during chlorination, have flavor thresholds of 0.48 mg/L and 0.13 mg/L respectively. Solutions of monochloramine elicit a chlorine-like flavor, while the flavor of dichloramine is often described as swimming pool-like or bleachy (AWWARF and LdE 1987).

In addition, chlorine as well as chloramines, chlorine dioxide, and ozone can interact with the organic compounds present in the water to produce by-products, some of which are known taste and odor-causing compounds. The most notorious by-products found in chlorinated waters are chlorophenols and trihalomethanes (THMs). Chlorophenols, which are formed when phenol and its homologous are chlorinated, emit chlorophenolic flavors. Compare to those of the original compounds, the detection flavor threshold values of chlorophenols are extremely low. For example, the identified flavor threshold of 2.4-dichlorophenol is 0.002 mg/L, while phenol has a value of 1.0 mg/L. Trihalomethanes can be detected by smell at 0.1 mg/L for chloroform and 0.3 mg/L for bromoform (AWWARF and LdE 1987).

Offensive odors at customer's taps associated with the use of chlorine dioxides during water purification have been described by terms such as strong chlorinous, kerosene-like, cat-urine-like, and fishy (Hoehn et al 1990, AWWARF and LdE 1987). The threshold odor level of chlorine dioxide in air at standard temperature and pressure is 0.0028 mg/L (Amoore and Hautala 1983). Hoehn et al. (1990) indicated that a chlorine dioxide residue of 0.2 mg/L or less is adequate to cause offensive odors.

Furthermore, Hoehn et al (1990) concluded that the strong chlorinous odor is caused by chlorine dioxide, which escapes from the water when the tap is opened. They also indicated that the volatilized chlorine dioxide can react with organic compounds in household air and produces an odor of a distinct kerosene-or cat-urine-like character.

Hoehn et al.(1990) did not specify the organic involved ; however, they postulated that new carpeting is a common source of the precursors.

Ozone is the most efficient oxidant in removing tastes and odors. Unfortunately, other taste and odor-causing compounds may be formed during ozonation. In a field study at the Morsang water treatment plant in France, ozone was found to be responsible for the development of high intensity fruity tastes and odors. These fruity taste and odors were correlated with the formation of aldehydes (Anselme et al. 1988).

3.1.4 Tastes and Odors Developed in Distribution Facilities

Despite the success of disinfection practices, regrowth of bacteria in some parts of distribution facilities often occurs. This activity may result in the degradation of organoleptic properties of the supplied water. The condition supporting the bacterial growth and the relationships existing between the number of microorganisms and the odor intensity are not fully understood. However, AWWARF and LdE (1987) postulated that the following conditions may be favourable for bacterial growth in the distribution systems : a high assimilable organic carbon (AOC) concentration, a high temperature, low water velocities in certain parts of the network, and prolonged residence times (more than 48 hours).

Corrosion of uncoated pipes and fittings containing iron, copper, and zinc may release appreciable amounts of these metals into the water. Biological activity of iron bacteria in the distribution network may be another source of iron. As mentioned previously, the unpalatable taste of iron can be detected at a concentration of 0.05 mg/L, while the astringent taste of copper and zinc can be recognized at concentrations of 3.5 mg/L and 5.0 mg/L respectively.

Lining and coating materials, which are suposed to protect the internal surface of pipes and tanks from corrosion, can contribute to the creation of tastes and odors in water. Leaching organic contaminants from these materials, such as naphthalene and polycyclic aromatic hydrocarbons (from bituminous), impart medicinal or pharmaceutical and solvent-like taste and odors. Other kinds of released organics can enhance the growth of bacteria (AWWARF and LdE 1987).

Organic solvents used during installation of coatings can contaminate the water. Leaching of tetrachloroethylene, a chlorinated solvent, has been observed to impart a medicinal taste and odor in the water (Stinson and Carns 1983). Krasner and Means (1986) reported that xylenes used during the construction of floating covers was leaching in considerable concentrations (greater than 0.02 mg/L) and creating an unacceptable taste and odor for a period of time (about 3 months). They, therefore, suggested that health and aesthetic factors have to be considered before newly coated reservoirs can be returned to full service.

Corrosion considerations have led to the extensive use of synthetic pipes, such as polyvinyl chloride (PVC) and polyethylene pipes, for drinking-water distribution. However, changes of drinking water organoleptic properties have been found in some cases. Anselme et al (1985) cited that three major causes for these changes are : dissolution of the polymer additive, oxidation of the internal surface of the pipe and dissolution of the resulting polar compounds, and migration of external contaminants through the pipes.

The use of high-density polyethylene (HDPE) pipes is motivated by a favourable material property, i.e. low permeability to external contaminants. In fact, this material releases numerous organic compounds associated with intense plastic tastes and odors. Anselme et al (1985) demonstrated that the occurrence of these tastes and odors is due to dissolution of the polymer additives (mainly alkyl phenols) and oxidation of the internal pipe surface during extrusion with subsequent release of the resulting polar compounds (mainly aldehydes). Furthermore, they indicated that the total release time may exceed several months under low flow conditions.

3.2. TASTE AND ODOR MEASUREMENT

Ideally, a taste and odor test involves both sensory and chemical analyses. Sensory analysis, which is done by the human sensory organs, provides qualitative descriptions and approximate quantitative measurements of taste and odor intensity (Standard Method 1989). As discussed earlier in Chapter 2, sensitivity to taste and odor varies from individual to individual, and even the same individual could be inconsistent in sensory testing from one day the next. This variation may lead to subjective results.

Chemical analysis, on the other hand, provides information on the occurrence of organic contaminants in the water sample. To be meaningful, the results must be interpreted in terms of human response. Therefore, relationships should be established between the organoleptic properties of the water and the concentration of the identified compounds.

3.2.1 Sensory Analysis

Sensory analysis can be classified into two categories : threshold and suprathreshold tests. The threshold tests, including threshold odor number (**TON**), threshold taste number (**TTN**), and odor intensity index (**DII**) tests, provide a dilution factor that represent the overall intensity of organoleptic perception. In the supra threshold tests, particulary flavor profile analysis (**FPA**) test, a water sample is tested without dilution and individual intensities of the perceivable contributors are recorded in a point scale system. Both the TON and FPA methods will be discussed in detail.

Threshold Odor Number Test (From Standard Methods 1989)

The threshold odor number, termed as **TON**, is represented by greatest dilution of odor-bearing water with odor-free water eliciting a definitely perceptible odor. The TON value is then calculated by dividing the total volume of the dilution sample by the volume of the odor-bearing water contained therein (eq. 3.1). Because the odor-bearing water is diluted before being tested, the TON method can be applied to a wide range of odorous-samples, from nearly odorless natural waters to highly odorous industrial wastes.

$$TON = \frac{mL\ sample + mL\ odor\text{-}free\ water}{mL\ sample}$$

Eq. 3.1 Threshold Odor Number

Sampling and Storage. Samples for odors testing should be collected in glass bottles with glass or TPFE-lined stoppers. To store the samples, glass bottles with at least a 500-mL capacity should be used, and the samples should be refrigerated without headspace in the bottles. If dechlorination is necessary, it can be done by adding stoichiometric quantities of arsenite or thiosulfate.

Temperature. Threshold odor values is significantly affected by temperature of the samples. The temperature at which samples should be tested can be as high as 60^0C, which may be necessary to detect odors that might otherwise be missed. A lower temperature, such as 40^0C, may be appropriate for odors that fade quickly or if excessive heat sensation tends to occur. The temperature at which the samples are observed should be reported.

Precaution. The panelists participating the TON test should carefully be selected to exclude those with low sensory sensitivity. The panelists should not have colds, allergies, and other conditions that might affect odor responses. The panelists should not use scented soaps, perfumes, or shaving lotions. The panellists should not smoke or eat (during the 15 minutes) before the test. The number of tests should be limited to avoid fatigue.

The testing room should be odor-free and free form other distractions. The glasswares should be cleaned with nonodorous agents and rinsed with odor-free water before use. Odorous glassware should be excluded. The use of opaque or brown flasks are recommended. On the other hand, the use of rubber, cork, or plastic stoppers should be avoided. The temperature of the samples should be maintained within 1^0C of the testing temperature.

Measurement. In principle, proper amounts of the odor-bearing water are added into separate 500-mL glass stopered flasks containing different amounts of odor-free water to make a total volume of 200 mL (various dilutions in Table 3.3 are suggested). Some blank samples containing odor-free water only are prepared as reference for comparison. The dilutions and blank samples are then heated to the desired testing temperature in a water bath or on an adjustable electric hot-plate. The flask should be shaken before its stopper is removed for sniffing test. Observations are recorded by indicating the response to each sample. As part of the test, the observers are asked to describe the characteristics of the odors.

A preliminary test employing 200 mL, 50 mL, 12 mL, and 2.8 mL of the odor-bearing water is suggested to determine the TON range. For example, if an odor is first detected (+) in the flask containing 50 mL of odor-bearing water, a series of dilutions containing 50 mL, 35 mL, 25 mL, 17 mL, 12 mL 8.3 mL, 5.7 mL, and 4.0 mL should be prepared for further test.

Table 3.3 Threshold odor numbers corresponding to various dilutions.

Sample Volume Diluted to 200 mL mL	TON	Sample Volume Diluted to 200 mL mL	TON
200	1	12	17
140	1.4	8.3	24
100	2	5.7	35
70	3	4	25
50	4	2.8	70
35	6	2	100
25	8	1.4	140
17	12	1.0	200

Source : Standard Methods (1989).

In some cases, anomalous responses occur, a low concentration in the series may be called positive (detected) and a higher concentration may be called negative. Therefore, the threshold is designed as the lowest concentration (or the highest TON) after which no further anomalies occur (Rosen et al. 1962). In the following example, a TON value of 8 should be assigned.

mL of odor-bearing sample diluted to 200 mL	50	35	25	17	12	8.3	5.7	4.0
Corresponding TON	4	6	8	12	17	24	35	50
Observation	+	+	+	-	+	-	-	-

Improvement of the results. Standards Methods (1989) emphasizes that the TON is not a precise value. The value can be improved if a panel of at least five members is involved in the measurement. The results derived by a panel is more meaningful because the effects of individual differences tend to have less influence.

However, TON measurement by a single individual is often a necessity at a water treatment plant. If this is the case, the relative acuity of the single observer is required to be calibrated, perhaps with a standard chemical, such as m-cresol or n-butanol. One or two observers can also provide useful data if their sensitivity has been assessed by a larger panel.

Potential Disadvantages. Most odors in natural waters are produced by chemical mixtures, which are present in different concentrations. Several phenomena, such as synergism, antagonism, and masking, may be involved. Therefore, the odors may be modified when the waters are diluted.

In practice, the TON assigned to a particular sample is determined by the most readily perceived chemical, which is not necessary the one that causes the characteristic odor of the undiluted sample. As a result, the TON may not be the threshold odor level of the compound or mixture of compounds causing the most intense odor. To be improved, the TON should be reported along with a description of the odor appearing at the dilution corresponding to the TON.

With the TON method, samples are heated to the testing temperature. In some cases, this procedure drives off volatile odorants so that only the first few observers can perceive the odors. To avoid this situation, a separate set of dilutions should be prepared for each observer. There could be logistical problems in providing all the necessary equipments, particulary odor-free glassware, that will be required.

Flavor Profile Analysis (FPA) Test

(Krasner et al. 1985, Bartels et al. 1986, Bartels et al. 1987, AWWARF and LdE 1987)

The flavor profile method was originally developed for food industry to completely describe aroma and flavor characteristics of a sample. This method relies on the judgment of trained panellists who also monitor each other's performance. Each panel member is periodically retrained and tested using objective reference standards .

The FPA method was initially adapted (with certain modifications) and pioneered for water treatment purposes by the Metropolitan Water District of Southern California (**MWDSC**) in 1981. The technique, which is applied to describe the organoleptic quality of raw and treated drinking water, has been used at the Philadelphia Water Department (**PWD**), the Philadelphia Suburban Water Company (**PSWC**), and the Lyonnaise des Eaux (**LdE**)-France since 1984. Currently, research on this method is directed to standardize certain elements of the method.

General principles. The flavor profile of a water sample is a compiled judgment about the aroma and flavor of the sample. The profile, which is made by a panel of four or more members, consists of a set of descriptions and sometimes notes, each with a respective intensity score. Although a panel leader coordinates the activity of the panel, he or she is not allowed to interfere with the way panellists make their decisions on description and intensity.

In the FPA test, a sample is simultaneously presented to the panellists. The individual records are then compiled by the panel leader. The panellists may discuss their records to obtain a more coherent description and a better agreement on the intensity of perceived aromas and flavors. Reference standards should be used to resolve any discrepancy between the panellists.

If the panellists remain with their descriptives, the following compilation should be done. If 50 percent or more of the panellists use the same descriptive, the intensity for this descriptive is calculated as the average of the individual intensity scores. In this calculation, an extreme intensity should be ignored. If less than 50 percent of them give a particular description, this description is recorded as a note of the respective aroma or flavor.

In the field of drinking water, a seven-point scale is used to score the intensity of aroma and flavor (Table 3.4). MWDSC uses the)(to 3 scale, with)(representing the threshold value, and intensity levels of 1/2 are used in between. PWD, PSWC, LdE, and Drexel University represent the threshold value with a number of 1 and use even numbers between 2 and 12 to represent higher intensities. Both scales are modifications of the original flavor profile test, where a four-point scale of)(, 1, 2, and 3 was used.

Table 3.4 Intensity scales at water utilities using the FPA method

Verbal Description	Intensity Scale Original FPA Test and MWDSC	Intensity Scale PWD, PSWC, and LdE
Threshold*	)(	1
Very slight	1/2	2
Slight	1	4
Slight to moderate	11/2	6
Moderate	2	8
Moderate to strong	21/2	10
Strong	3	12

Note : * The value of intensity that represents an odor or flavor just perceivable by a panelist or that perceived by 50 percent of the panel. In the)(to 3 scale,)(is ploted as 1/4.

Source : AWWARF and LdE (1987).

Selection and Training FPA Panellists. Although factors, such as education level or knowledge of water treatment, are postulated not to pose limitations for selecting panellists, the following requirements should be considered. A panelist should be able to express his/her findings verbally and should be assertive about these findings, even if he/she is in the minority. In addition, a panelist should be interested to participate the panel and should be available over a long period of time. Moreover, a panelist should have moderate to high sensitivity for various odors found in water and should have good odor recognition ability.

Like the FPA method itself, panel training can be modified for special needs. However, there are two categories of training, i.e. initial and continuous training, that should be participated by panellists. Initial training involves understanding the senses and developing basic skills. MWDSC experienced that good results can be gained after a three-day initial training of approximately 20 hours.

Continuing this training, panellists are given the opportunity to participate regular panel sessions. Additional training, which consists of exposing panellists to standards and samples, is also provided as a part of continuous training. The total training period takes several months if meetings are scheduled once a week. After this period, every panelist should be involved in a panel at least once every two weeks so that his/her sensory skills can be maintained at a high level.

Sampling and Storage. Samples are collected in 1-L or 1-gal glass bottles that have been washed, rinsed with acetone, dried with air, and baked at 180^{0}C overnight. The bottles are rinsed with sample water before being filled and capped with PTFE-lined caps. Headspace is kept as small as possible. The samples are stored in an ice chest during transportation to the laboratory, where they are refrigerated at 4^{0}C. The samples should be analyzed as soon as possible (within 24 hours of sample collection). Dechlorination is not necessary since chlorine is often a source of taste and odor problems. In addition, some dechlorinating agents are toxic to drink, and some can produce their own off-tastes.

Temperatures. The temperature at which samples are smelled depends on the preference of the panel. At MWDSC, samples for aroma and flavor testing are heated to 25^{0}C in a water bath for 15 min prior to analysis. The odors of interest may be more detectable at a higher temperature; therefore, a temperature of 45^0C has been used at PWD, PSWC, and LdE. At this temperature, however, MWDSC finds that glass bottles impart a chalky odor and plastic cups produce an objectionable plastic aroma. In addition, some volatile odorants may be lost at 45^0C so that they may only be present for the first sniff. Some experimentation may be necessary to determine which temperature is best for conducting the evaluation.

Containers for aroma and flavor analysis. The type of containers in which the samples are presented for aroma analysis depends on the testing temperature. If samples are to be smelled at 25^0C, either disposable plastic cups (200 mL size) or Erlenmeyer glass-flasks (500 mL size) can be used. It is necessary to note that the plastic odor of a plastic cup can interfere with floral odors and chalky odor of a glass-flask can interfere with low-level musty odors. If aroma analysis is conducted at 45^0C, Erlenmeyer glass-flasks are recommended, instead of plastic cups.

Flavor analysis is done at 25^0C. Plastic and glass containers that impart little or no flavor to the sample are, therefore, suitable for the analysis. Whatever slight flavor might be imparted to the sample, it must be tuned-out by the use of a proper control.

Testing Conditions. The panel should be held in a clean, well-lit, quite, odor-free, and temperature-controlled room. The panellists should sit around a common table so that they can share results and discuss their responses. A blackboard or an easel pad should be provided in the room. The use of markers with strong solvent-type odors must be avoided.

Panellists who are going to be used in the panel should be confirmed in advance. Panellists who have colds or allergy flare-ups the day of the evaluation should report this condition so that a substitute can be found. The panellists should not smoke or eat for 15 to 30 min before the panel session. They should not wear perfume or cologne the day of the session, and they should wash their hands with a non-odorous soaps before beginning the evaluation.

Evaluation procedure. The samples are brought to the testing temperature in a water bath (at 25^{0}C for 15 min or at 45^{0}C for 20 min). For each panelist, a proper amount (60 mL if using a plastic cup or 200 ml if using glass-flask) of the sample is placed in the properly prepared or acceptable disposable container. The filled container is then covered (with a watch glass or a glass stopper) and swirled for a few seconds or shake five times in up-and-down motion to release odors into the airspace above the sample. Next, a few quick sniffs of the sample are taken. As soon as the sample is smelled, the results (descriptions of perceived aromas in the sample and their respective intensities) are recorded as the individual results.

Only samples that are known to be biologically and chemically safe are subjected to flavor analysis. At MWDSC, raw water samples are first filtered with a 0.45-µm filter to remove microorganisms. At LdE, a 0.20 µm filter is used for the same purpose. This sterilization is not adequate to remove viruses, but these are not a problem at

MWDSC and LdE. Some raw-water samples are irradiated with ultraviolet light. Sample that have a hydrogen sulfide or septic odor should only be smelled. Samples for flavor analysis should be brought to 25°C before they are poured into the containers. The results are recorded immediately after tasting.

Compilation of the results. After completion of individual study of a sample, the panel leader writes the panellists' results on a blackboard or easel that can be seen by everyone. Based on the order of appearance, description, and intensity, the responses are grouped along with soliciting comments from the panellists. Finally, the general procedures of compilation (as described previously) are applied to develop the flavor profile of the sample.

Goals for standardizing the FPA method. To provide reproducible and valid information on taste and odor problems in drinking water, certain elements of the FPA method needs to be standardized. These elements include manuals for conducting the method, training the panellists, building data sets of frequency occurring problems, and validating the FPA by cross-comparison of the results. Further standardization of the FPA method is directed toward developing knowledge about the origin of taste and odor problems by statistical and mathematical techniques.

A list of reference standards is one of the important parts of the manuals. Currently, the FPA method allows panellists to use a large number of descriptives for characterizing water samples. This flexibility makes panel results difficult to be compared. A preliminary list of descriptives for possible standard compounds (Table B.1 in Appendix B) is under development at PWD. This list is far from complete because some of reference compounds for common aromas and flavors in drinking water are not available.

Disadvantages. A panel of four or more members is an integral part of the FPA method. Setting up a skilled panel for FPA test requires several steps, such as selecting and training panellists, which takes time and effort. To be consistent in detecting off-flavors, available trained panellists should also be used frequently, preferably on a rotating basis. Therefore, maintaining an expert panel over a long period of time could be impractical, particulary for small utilities.

Reference compounds are absolutely required for selecting and training panellists and during regular panel sessions. However, some of these compounds are not available and some should be prepared in a low concentration (e.g. a few nanogram-per-liter) by using sophisticated equipment. It is not always practical or possible to satisfy this requirement, particulary in small utilities.

3.2.2 Chemical Analysis

A very sensitive analytical method is required to identify and quantify the occurrance of trace organic contaminants in natural water. Numerous different organic compounds are found in natural water and many of them, such as geosmin and MIB, are typically present at a few nanogram-per-liter. The method, therefore must have a high discriminatory capability and a low detection limit. The most suitable method for these purposes is capillarity gas chromatography for the separation of the compounds followed by mass spectrometry for the identification of the compounds (GC/MS).

General Principles

(from McGuire et al. 1981, AWWARF and LdS 1987, and Standard Methods 1989)

The GC separates the organics based on the difference in partition coefficient between the mobile and stationary phases (the carrier gas and the column packing respectively). Each component of the organics can be passed through a flame ionization detector (**FID**) or an electron capture detector in which a quantitatively proportional change in electric signal is measured. The resulting chromatogram is then recorded and processed by an integrator. The retention time, i.e. the time between injection and detection, is an indicator of a particular organic compound. The peak high and peak area are proportional to the concentration.

If concentration of the isolated solutes are large enough (more than 20-50 ng/L), the compounds can be analyzed by MS. In the mass-spectrometer, the compounds are ionized into charged species. The ions are then accelerated toward a mass filter through a series of electromagnetic fields. The different sized and charged fragments are separated according to the ratio of mass-to-charge. Finally, the resulting fragmentation pattern is compared to known mass spectra to identify and quantify the unknown compounds.

Prior to the GC/MS or GC/FID analysis, the organic compounds of the interest have to be isolated from the water phase. The isolation technique should not modify the organic compounds present in the sample, should recover all organics from the water, and should completely recover these organics from the previous phase. At present, these requirements can only be approximated because the typical recovery level is 70 percent. Several techniques are available for compound isolation.

Liquid-Liquid Extraction. Liquid-liquid extraction (**LLE**) is based on the extraction of nonvolatile and semivolatile organics using a suitable organic solvent. The extracted organics should be concentrated before they are analyzed by GC/MS or GC/FID. This technique has widely been used because of its simplicity. However, the high detection levels of this technique (5 to 10 µg/L) may limit its application to geosmin and MIB.

Closed-Loop Stripping Analysis. Closed-loop stripping analysis (**CLSA**) can be used to isolate nonpolar-(semi)volatile organic compounds of intermediate molecular weight. These compounds are stripped from the water by a recirculating stream of air. The organics are removed from the gas phase by an activated carbon filter. Subsequently, the organics are extracted from the filter with carbon disulfide (CS_2). The isolated extract is then injected into a GC for separation of the individual compounds. The use of CLSA-GC allows the determination of taste-and-odor causing compounds like geosmin and MIB at level of 3 to 10 ng/L with FID and 1 ng/L with MS detection.

Steam Distillation Extraction. Steam distillation extraction (SDE) is a gas phase liquid-liquid extraction performed during 3 hours under reflux condition. In principle, three liters of water sample and 50 mL of CH_2Cl_2 solvent are heated separately. The sample vapour, which consists of the steam and steam-distillable organic compounds, is mixed with the solvent vapour in a distillation-extraction head. The mixed vapour is then condensed together. The condensate separates into two phases, the extracted organics and the solvent. Subsequently, the extracted organics are subjected to GC/MS or GC/FID analysis.

SDE is considered as a supplement to CLSA because SDE isolates a different matrix of organics than CLSA. SDE has been found to be more effective than CLSA in collecting organic compounds with higher molecular weights (many of which are highly odorous) and higher polarities. SDE, therefore, widens the detection range of taste-and-odor causing organics. The use of SDE in conjunction with CLSA may provide better associations between these compounds and organoleptics characteristic of the water.

Relation between Chemical and Sensory Analyses

There is, at present, no comprehensive and generalized method for integrating data obtained from chemical and sensory analyses. The problem stems from the fact that the chemical phenomena, such as interactive, synergistic, and antagonistic effects, in complex mixtures of odorant compounds at or below individual odor thresholds have not been fully understood. Nevertheless, the following methods can be examined.

It has been postulated that relationships exist between chemical concentration and odor intensity, as well as between a chemical and its corresponding odor quality. The Weber-Fresner law of olfactory sensation (1859) states that odor intensity perceived has a semilogarithmic relationship with the concentration of the taste-and-odor causing chemical. Krasner et al. (1985) demonstrated that in pure MIB solution and with a specific concentration range, a linear response was obtained for the flavor-profile intensity score and the logarithm of the concentration. However, AWWARF and LdE (1987) found that simple functional models, such as a semilogarithmic response, could not be implemented under different conditions.

AWWARF and LdE (1987) developed a predictive organoleptic model-stochastic regression, which was applicable to a data base developed in the laboratory. This model was also used to simulate flavor profiles from fictitious chromatograms. In addition, the model offers a practical and precise method for analyzing the influence of certain compounds on the organoleptic quality of waters. However, the existing data base must be enlarged to verify the model.

3.3 TREATMENT OF TASTES AND ODORS IN POTABLE-WATER SUPPLIES

Taste and odor control is often complicated by the inability of providing sufficient information about the nature of the problems and the available treatment techniques. Several stages of investigation may be critical if the problems need to be fully characterized. These components include sanitary survey for the identification of land-use of watershed areas, waste dischargers, runoff patterns, and lake and reservoir stratification; sensory evaluations for the determination of the various types and intensities of tastes and odors; microbilogical investigations for the identification of organisms causing the problem; and chemical analysis for the isolation and identification of the causative compounds. Simple problems can be solved with any three, possibly even two, of these components.

The available literature can indicate types of successful treatment schemes applied by other utilities. Information on both the value and shortcomings of different techniques for taste-and-odor control exists in a variety of references. The following material is presented as examples of what treatment may be performed.

3.3.1 Preventive Measures

Water Pollution Control. As discused previously, anthropogenic activities can directly or indirectly create taste and odor problems. Water pollution control programs in watershed areas of the supply sources is, therfore, necessary. These programs may involve stream-monitoring programs, routine-sanitary surveys, agricultural-land management, and waste management. These efforts are tedious, but the results can be very rewarding.

Actinomycetes control. One branch of taste and odor control is, of course, the control of odorant producing microorganisms. Generally, no chemical control for actinomycetes in rivers, lakes, or reservoirs, is suggested. Copper compounds, chlorine, and even arsenicals have been attempted with little or no success (Silvey et al. 1950 and Romano and Safferman 1963). Although sodium chlorite application will eradicate actinomycetes of the genus Streptomycetes, it is not a wise practice since the water in the reservoirs will not be consumed in one season.

Algicides. Many algicides have been used to limit the growth of odor producing algae. **Copper sulfate**, the most common algicide, was first used as an algicide in 1904 (Wolman 1956). To be effective, copper sulfate must contact the algae in a sufficient concentration. The most critical factor in using this algicide is, therefore, the application procedure (i.e. the rate, timing, and location of copper sulfate application). Smaller crystal sizes tend to dissolve before sinking to the bottom, so that surface application of this type should not be done to control algae that are attached at the bottom of deep reservoirs. In addition, copper sulfate will react with carbonate alkalinity to form copper carbonate, hence, an additional dose of copper sulfate is required.

Medium size chunks (6-13 mm) of copper sulfate were reported to be effective for controlling growths of attached blue-green algae in Lake Mathews-Southern California (McGuire et al. 1984 and Means and McGuire 1986). The application of cooper sulfate involved a heavy duty chemical spreader to facilitate the desired rate, CLSA-GC/MC analysis to determine the proper time, and divers to identify the target application areas. Copper sulfate effectively killed the blue-green algae and curtailed the taste and odor episodes. However, the organisms rapidly recolonized the treated areas. This resulted in a second peak of the MIB concentration in the lake (about two months after the first peak).

Copper sulfate may be toxic to other biological forms. American Water Works Association and Manitoba Water and Waste Association (1992) noted that fourteen hundred parts-per-million of copper sulfate will kill trout and thirty-three hundred parts-per-million will kill carp. Care must, therefore, be taken not to overdose.

Copper sulfate has often been found ineffective for controlling the growth of algae (Ringer and Campbell 1955, Bean 1957, and Valcik 1975). Moreover, a high content of copper sulfate in the finished water may be undesired, particulary by specific industries. Copper sulfate is, therefore, considered to be a partial solution to the associated odor problems.

Chlorine dioxide has been reported to be a more effective algicide than copper sulfate. Chlorine dioxide will oxidize the chlorophyll of algae. As a result, plant metabolism for protein synthesis will be interrupted and plant cell will be damaged to the point where loss of water from the protoplasm brings about hypertonic shrinkage. This irreversible process, termed as plasmolysis, will cause the algae to die. Moreover, this process is postulated to render their essential oils tasteless and odorless (Ringer and Campbell 1955). In addition to the high cost of chlorine dioxide, concern over the formation of chlorites, inorganic by-products, may limit its application to surface waters.

Surface Water Sources Aeration. Diffused air aeration can be used to control the occurance of taste and odor in lakes, reservoirs, or impoundments. Aeration promotes a mixing or a circulation action that may cause biological and microbilogical changes to occur. In turn, this action can result in reduction of algal growth. Aeration will also provide additional oxygen that is necessary to prevent septic conditions and to a limited extent, for oxidation of organic matter. Moreover, aeration can be used to release taste and odor producing substances (such as hydrogen sulfide) and to a limited extent, volatile organics (such as naturally occuring odorous compounds). However, aeration has often been considered ineffective.

3.2.2 Corrective Measures

Taste and odor control can be extremely complicated or very simple, depending on a variety of factors. However, the following factors should be considered for incorporating treatment methods into design. Taste and odor treatment should not promote the formation of undesirable by-products. Treatment chemicals should be applied in a way that minimizes antagonistic interactions among the chemicals. Flexibility should be provided as much as possible to allow for changing conditions. In practice, successful treatment will rely on frequent testing, adequate operation, and an adequate monitoring program.

In-plant control of tastes and odors may involve aeration, coagulation, oxidation, and adsorption processes. In many cases, combinations of two or more of these processes are required. As summarized by AWWARF and LdE (1987), the AWWA Water Quality Division (1983) reported that the most frequent method used to control tastes and odors in 1978 in the United States was powdered activated carbon adsorption (52 percent of 279 respondents). Potassium permangante oxidation was the next (26 %). Seventeen percent of the respondents listed ammonia oxidation, and twelve percent of them utilized chlorine dioxide oxidation. None reported using ozone oxidation. Another survey may provide a different composition, as tastes and odors vary widely at different times.

Aeration

Aeration can be defined as the process of bringing water into contact with air in order to expedite the transfer of a gas between the two phases (Cornwell 1990). This process, which can be done by bringing water through air or injecting air through water, serves as two treatment processes, i.e. oxidation and air stripping. With oxidation, the taste-and-odor causing compounds are oxidized into innocuous products that can be removed from the water. An example of this process is the use of aeration to oxidize iron and manganese.

In general, air stripping will remove volatile compounds that may be present in raw or treated water. AWWARF and LdE (1987) indicated that this process is effective for compounds that have a Henry's law constant greater than 10^{-3} m^3 atm/mol. Lalezary et al. (1984) indicated that air stripping is economically unfeasible for removal of four earthy-musty odorant compounds (IPMP, IBMP, MIB, geosmin) as their Henry's law constant are in the range of 10^{-5} m^3 atm/mol. A good removal of some volatile organic compounds, such as toluene (methyl benzene), ethylbenzene, 1,4-Dichlorobenzene, naphthalene, and trichloroelthylene, by aeration can be expected (AWWARF and LdE 1987 and Lalezary et al. 1984). Air stripping is also known to be effective for the removal of hydrogen sulfide (H_2S) from water.

Coagulation

Coagulation is traditionally a pretreatment process for removing gross particulates. However, many studies have demonstrated that it can also reduce the concentration of naturally occurring organics, including humic and fulvic acids. The effectiveness of natural organic matter removal by alum coagulation is mostly influenced by alum dose and pH (Semmens and Field 1980). Organics removal increases with increasing alum dose, and alum doses higher than those normally required for turbidity removal are needed to achieve the best organics removal. The optimum conditions for turbidity removal are not always the same as the optimum conditions for organics removal. Nevertheless, good organics removal always coincides with good turbidity removal. Therefore, pH of 5-6 is suggested for the best organics removal.

Randtke and Jepsen (1981) reported that the degree of organics removal is also related to the inorganic composition of the water and the type of organic matter present. The occurrence of certain cations, such as calcium and magnesium, improves the organics removal. Furthermore, coagulation preferentially removes either strongly or weakly adsorbing organic molecules. At this level of understanding, it is supposed that naturally occurring odorous compounds can effectively be removed by coagulation.

More recently, Randtke (1988) postulated that the type of organic contaminants will also affect the performance of coagulants. Randtke indicated that coagulation tend to remove organic compounds which are naturally hydrophobic, having a high molecular weight, and possesing functional groups which result in their adsorption onto floc particles. Fortunately, coagulation is generally found to preferentially remove color, THM and TOC precursors, and large molecules that are adsorbed poorly on granular activated carbon. Nevertheless, Semmens et al. (1986) concluded that aluminum will not improve carbon adsorption until a certain alum dose has been applied.

Oxidation

Oxidation of taste-and-odor causing compounds includes the application of chlorine, chlorine dioxide, potassium permanganate, and ozone. Unfortunately, chlorine, chlorine dioxide, and ozone may also cause some taste and odor problems (consider section 3.1.3). Recent studies by Lalezary et al. (1986), Anselme et al. (1988), and Glaze et al. (1990) demonstrate that chlorine, chlorine dioxide, and permanganate are not effective in reducing MIB and geosmin. Dispite this experimental evidence, there has been anecdotal evidence. These oxidants should, therefore, be considered as a possible option.

Chlorine. Heavy doses of chlorine can occasionally control taste and odor problems originating from algal metabolites (Ettinger and Middleton 1956). In addition to the fact that chlorine can intensify other odorous compounds, the formation of trihalomethanes

(THMs) in chlorinated waters has forced water utilities to reexamine chlorination practices. Chlorine is, therefore, unlikely to be a viable alternative in taste and odor control.

Chlorine Dioxide. With a higher oxidizing power, chlorine dioxide is considered superior to chlorine, particularly for taste and odor control. Chlorine dioxide does not combine with ammonia to produce chloramines nor with natural organics to form trihalomethenes. In addition, chlorine dioxide is very effective in the destruction of phenolic compounds without creating taste-and-odor causing compounds. However, concern over the formation of chlorites, inorganic by-products (Aieta and Berg 1986), may limit its application to surface waters.

In 1956, Ettinger and Middleton identified that about 100 treatment plants in the United States were utilizing chlorine dioxide to control difficult taste and odor problems. In the last 15 years, the use of chlorine dioxide in the United States municipal water supplies has declined significantly. As mentioned previously in this section, the AWWA Water Quality Division (1983) reported that only 34 utilities (12 percent of the respondents) were using chlorine dioxide in 1978.

In some cases, chlorine dioxide has failed to alleviate such problems of taste and odor. Besozzi and Vough (1949), for example, reported that chlorine dioxide used at the Whiting Indiana plant did not effectively reduce the threshold odor number of the water. Furthermore, Shull (1962) reported that chlorine dioxide failed to remove the musty-woody tastes and odors imparted by microorganims in Crum Creek water in Philadelphia.

Recently, Walker et al. (1986) reported that chlorine dioxide employed at the Rossdale Edmonton plants had eliminated the naturally occurring organics (earthy, musty, and fishy tastes and odors), presumed to be the metabolites of certain actinomycetes and algae. The use of chlorine dioxide has also removed the chlorophenols formed by naturally occurring organics, but it has not destroyed the taste or odor of certain hydrocarbons originating from urban runoff. Finally, they concluded that complete removal of taste and odor problems in the plants depends on the implementation of fixed-bed activated carbon treatment.

Potassium Permanganate. Many water utilities have relied on the use of potassium permanganate as an adjunct to powdered activated carbon for controlling their taste and odor problems. Cherry (1962), for example, reported that during a severe musty-earthy-septic odor episode in July 1961, Cedar Rapids Iowa applied 10.1 mg $KMnO_4$/L with 30 minutes reaction time to reduce the threshold odor of the raw water from 896 to 68 (or 92% reduction). This improvement involved the elimination of all the coagulants from the primary mixers so as to provide a greater contact time with permanganate alone. Maloney (1968) reported that potassium permanganate has reduced the threshold odor of Des Moines' raw water from 25 (or less) to a satisfactory level. Maloney also stated that the odors were typically of an earthy or musty character, but Maloney did not specify the dosage and contact time applied to the raw water.

The reactivity of permanganate in water, as reflected by the rate and extent of permanganate consumption, is governed by the pH of the solution, raw water quality, permanganate dose, and allowable reaction time. Singer et al. (1980) indicated that permanganate is appreciably more reactive at higher pH values. They demonstrated that the reactivity of permanganate also depends on the nature of organics constituting the TOC in the water. They indicated that permanganate is more reactive to organic substances that are more soluble and having lower molecular weight. Finally, they noted that permanganate is more reactive at higher dosages.

Ozone. In general, ozone is a powerful oxidant that has been used by many water plants for taste and odor control. The Whiting Indiana plant has been an example of a small ozone installation (Bartuska 1941). A larger installation has been operated at the Belmont plant Philadelphia. At this plant, the effectiveness of ozone to split musty odors has been demonstrated, although ozone has been found more effective on industrial waste materials (Bean 1957). One of the reasons that ozone has not been used more widely in the United States is a high capital investment required for generation equipment. The other reason is that very high dosages are needed to maintain a high ozone residual, otherwise it will disappear in a very short period.

Recent Studies. A study by Lalezary et al. (1986a) compared the effectiveness of chlorine, chlorine dioxide, permanganate, and ozone for the destruction of five earthy-musty taste and odor compounds. The study showed that the two major forms of earthy-musty taste and odor organics, MIB and geosmin, are resistant to oxidation. For example, an impracticable dose of chlorine (20 mg/L) reduced geosmin from 120 to 80 ng/L (25 percent removal) after a 16-h contact time. With a dose of 4 mg chlorine dioxide-per-liter for the same contact time, the removal was somewhat better (45 percent), but there was no additional removal at dosages larger than 4 mg/L. Potassium permanganate did not oxidize geosmin under the condition used (2-h contact time, up to 50 mg/L dose). Low dosages of ozone were moderately effective (20 percent removal of geosmin at 2 mg ozone/L), but an unexpected decrease in removal effeciencies at larger than 4 mg/L were observed. The water used in this study was a highly purified water.

Different results may be obtained when the oxidants are applied to natural waters that contain many organic pollutants. A study by Anselme et al. (1988), that used a natural water, demonstrated a better performance of ozone in oxidizing the earthy-musty-muddy odorant compounds. However, no data was obtained on MIB or geosmin.

More recently, the work of Glaze et al. (1990) showed that coventional oxidants, such as chlorine, chloramine, chlorine dioxide, and permanganate can not control the occurrance of taste and odor problems in water supplies that are caused by MIB and geosmin. However, Glaze et al. found that ozone is capable of oxidizing MIB and geosmin. They postulated that this evidence is due to the OH radical resulted from the reaction of ozone and constituents in natural waters. Finally, they noted that further studies are necessary to elucidate the exact mechanism involved in this evidence.

Activated Carbon Adsorption

Activated carbon removes organic contaminants from water by the process of adsorption or the attraction and accumulation of one substance on the surface of another. This process is reversible, i.e. organic molecules continue to accumulate on the surface of activated carbon until the rate of adsorption equals the rate of desorption. When this condition exists, equilibrium has been reached and no further accumulation will occur.

Physical adsorption on activated carbon involves four steps (Snoeyink 1990). First, adsorbates (molecules being accumulated) are driven from bulk solution to the boundary layer of water surrounding the adsorbent particles (adsorbing solids). This step, termed as bulk solution transport, occurs by diffusion if the adsorbents are suspended in quiescent water (such as in a sedimentation basin) or by turbulent mixing (such as in a packed bed contactor or in a mixing basin). Second, the adsorbates are driven by molecular diffusion through the stationary layer of water that surrounds the adsorbents (film diffusion transport). Third, the adsorbates are driven by molecular diffusion to available adsorption sites inside the pores and along the surface of the adsorbents (pore transport). Finally, the adsorption bond is formed between the adsorbate and the adsorbent (adsorption). The longest step will determine the adsorption rate.

Isotherm Equilibrium. An adsorbent may be characterized by the amount of adsorbates that can be accumulated. The equilibrium relationship between the amount of adsorbed (x) per unit weight of adsorbent (m), $q_e = x/m$, and the equilibrium concentration of adsorbate in solution, C_e , at a given temperature is defined as the adsorption isotherm. The most accurate formula to express the adsorption isotherm is the Freundlich isotherm (Eq. 3.2).

$$q_e = K\, C_e^{1/n}$$

or

$$\log q_e = \log K + \frac{1}{n} \log C_e$$

Eq. 3.2 Freundlich Isotherm

The Freundlich isotherm is a linear relationship between the logarithm of q_e and the logarithm of C_e. The constant K is primarily related to the capacity of the adsorbent for the adsorbate, and 1/n is a function of the strength of adsorption. The Freundlich equation is no longer applicable whenever saturation condition, at which the q_e is constant and independent of further increases in C_e, is achieved.

Factors Affecting Adsorption Equilibria. An adsorption isotherm is influenced by several factors, including the nature of the adsorbent, the nature of the adsorbate, the nature of the solution, and the contacting system. The adsorption capacity of adsorbent is proportional to the amount of surface area within the pores that is accessible to the adsorbate. The surface area directly corresponds to the pore volume. In addtion, the pore size distribution dictates the molecule size and the amount of the adsorbate that can penetrate into the pores.

The particle size of adsorbent significantly affects the adsorption rate because it determines the time required for transport within the pore to adsorption sites. Calculations done by Randtke and Snoeyink (1983) illustrated that a decrease in the particle size results in a higher adsorption rate. When the same carbon dosage was used for the removal of dimethylphenol (molecular weight = 122), the estimated time to reach equilibrium was less than 15 min for 325-mesh-size (44-µm) carbon compared with about 13 h for 30-mesh-size (595-µm) carbon. Batch adsorption tests conducted by Najm et al. (1990) confirmed this trend and also demonstrated that particle size has no effect on adsorption capacity.

In combination with the characteristics of the adsorbate, the surface chemistry of the adsorbent can also affect the extent of adsorption. Snoeyink (1990) noted that extensive oxidation of the activated carbon with ammonium persulfate or chlorine was found to decrease the adsorption capacity for phenol. Snoeyink also cited that increased amounts of surface oxygen decreased the affinity of carbon black for benzene. Finally, Snoeyink concluded that oxygeneted surfaces do not adsorb at least simple aromatic compounds strongly.

The amount of adsorption is governed to some extent by the solubility of the adsorbate in water. Snoeyink (1990) cited that adsorption onto GAC from water generally increases as the adsorbate's solubility decreases. Snoeyink also noted that the presence of hydrophobic (water disliking) groups such as $-CH_2-$ in a molecule decreases the solubility of the molecule and increases its extent of adsorption as long as the molecule can penetrate into the pores. However, as molecular size approaches the adsorbent's pore diameter, the rate of diffusion within the pores decreases.

The affinity of weak organic acids and bases for activated carbon is dependent upon the pH of the solution. Sawyer and McCarty (1978) reported that the adsorption capacity of activated carbon is relatively high when the pH is in a range where the molecule is in the neutral form. When the pH is in a range where the molecule is ionized, affinity for water is very high and activated carbon capacity is accordingly very low. In addition, The pH of the solution affects the charge on the adsorbent surface, altering its ability to adsorb materials.

The inorganic composition of water can also influence the extent of adsorption. Randtke and Jepsen (1982) concluded that calcium, magnesium, and sodium salts enhance the adsorption of fulvic acids on activated carbon, with calcium being the most effective. However, excessive deposition of inorganic substances, such as iron, manganese, and calcium salts, on the adsorbent may decrease the extent of adsorption (Snoeyink 1990).

Competitive adsorption is of importance because most compounds to be adsorbed exist in solution with other adsorbable compounds. The extent of competition on activated carbon depends upon the adsorption strength of the competing molecules, the concentration of these molecules, and the type of activated carbon. Herzing et al. (1977), for example, reported that the presence of 10 mg/L of a humic substance reduced the capacity for geosmin by about 90 percent at an equilibrium concentration of 1 mg/L. Using a different humic substance, Lalezary et al. (1986b) found much less reduction. The adsorbability of competing molecules in natural water varies widely; therefore, wide variation in the extent of competition is expected.

Adsorption Properties. A number of parameters can be used to express the adsorption properties of activated carbon. The molasses number or decolorizing index is associated to the ability of activated carbon to adsorb large-molecular weight color bodies from molasses solution, and generally correlates well with the ability of activated carbon to adsorb other large adsorbates. The iodine number measures the amount of iodine that will adsorb under a specific set of conditions, and generally correlates well with the surface area available for small molecules. Other parameters were developed for specific applications, such as the carbon tetrachloride activity, the methylene blue number, and phenol adsorption value.

Powdered Activated Carbon. The primary property that differentiates powdered activated carbon (**PAC**) from granular activated carbon (**GAC**) is the particle size. Commercially available PACs typically show 65 to 90 percent passing a number 325 mesh sieve (44-µm). The apparent density of PAC, i.e. the mass of non-stratified dry activated carbon per unit volume of activated carbon (including the volume of voids between grains), ranges from 0.36 to 0.74 g/mL.

Adsorption with activated carbon, either in the powdered or granular form, has been considered the most effective treatment for taste and odor problems. Powdered activated carbon was first applied for this purpose in 1930. Twenty-six years later, over 1,200 water treatment plants in the United States were identified using PAC (Wolman 1956). The Cedar Rapids and Des Moines treatment plants in Iowa have been two of those that rely on the use of PAC in conjunction with potassium permanganate (Cherry 1962 and Maloney 1968). Recently, Burlingame et al.(1986) reported that PAC was successfully utilized to control the occurrence of geosmin at the Belmont plant in Philadelphia. A dose of 42 mg PAC/l reduced this earthy-smelling substance by about 73 % (from 67 to 16 ng/l).

As discused previously, many factors may interfere with the extent and the rate of activated carbon adsorption for the removal of specific compounds. A study by Lalezary et al. (1988), for example, indicates a marked decrease in PAC adsorption of geosmin and MIB in the presence of background organics. Furthermore, this study demonstrates that chlorine and chloramine manifest a distinctly adverse effect on the PAC adsorption capacity of geosmin and MIB.

Floc particles may also reduce the adsorption rate of PAC because the adsorbates must diffuse through the part of the floc surrounding the PAC particle before they diffuse into the particle pores. The addition of PAC after floc formation, to some extent, provides a better removal rate than before floc formation. This is because PAC added after floc formation adheres to the outer surface of the floc rather than being incorporated into the floc (Snoeyink 1990).

Generally, the effectiveness of PAC for taste and odor control depends on several design and operational parameters. The point of PAC application should, therefore, be arranged in a way that ensures a good mixing or a good contact between the PAC with all of the flow, a sufficient time of contact with the contaminants, a minimal interference by the other treatment chemicals, and no degradation of finished water quality. Regarding these criteria, Snoeyink (1990) summarized some of the advantages and disadvantages of different points of PAC application (Table 3.5).

Table 3.5 Advantages and disadvantages of different points of PAC addition

Point of addition	Advantages	Disadvantages
Intake	Long contact time, good mixing	Some substances may adsorb that otherwise would be removed by coagulation, thus increasing the carbon usage rate.
Rapid Mix	Good mixing during rapid mix and flocculation, reasonable contact time	Possible reduction in the rate of adsorption because of interference by coagulant. Contact time may be too short for equilibrium to be reached for some contaminants. Some competition may occur from molecules that otherwise would be removed by coagulation.
Filter inlet	Efficient use of PAC	Possible loss of PAC to the clear well and distribution system.
Slurry contactor preceding rapid mix	Exelent mixing for the design contact time, no interference by coagulants, additional contact time possible during flocculation and sedimentation	A new basin may have to be installed. Some competition may occur from molecules that otherwise would be removed by coagulants.

Source : Snoeyink, V. L. (1990).

The primary advantages of using PAC, other than its effectiveness, are its low capital investment and its flexibility compared to the other processes for treating the sporadic occurrance of taste-and-odor causing compounds. However, many concerns have been attributed to the use of PAC for water purification. Typically, the point of PAC application provides inadequate opportunity for utilization of the adsorption capacity of the activated carbon. Unfortunately, this unsaturated carbon is difficult to reuse. In addition, PAC can only remove a small portion of the total organic carbon (TOC). Sludge disposal may become a serious problem, especially when the PAC has adsorbed certain toxic substances or their precursors. Moreover, PAC particles are difficult to be completely removed from the water. These concerns may force water utilities to exclude PAC in their treatment facilities.

Granular Activated Carbon. Granular activated carbon (GAC) should be seriously considered for water purification when acceptable removal of taste and odor compounds or other potential contaminants cannot be obtained by conventional means or even PAC. GAC columns perform as plug-flow reactors that provide favourable conditions for efficient utilization of the adsorption capacity of the carbon. GAC beds are also able to justify different applied-water quality, so that they permit simple operational control. In addition, the exhausted carbon can be removed from the beds for reactivation and reuse, which may result in lower over-all costs. GAC, moreover, has excellent adsorption capacity for many undesirable substances, such as volatile and synthetic organic compounds, radionuclides, inorganic compounds, and disinfection by-products

(DBPs) (Oxenford and Lykins Jr. 1991). These advantages confirm postulations that GAC would be a viable technology for removing many impurities from water.

The important properties of GAC other than specified previously are the apparent density, the bed density backwashed drained, the particle density wetted in water, and the particle hardness. The apparent density characterizes GAC at dellivery. The bed density backwashed drained, which is about 10 percent less than the apparent density, is typical of GAC during normal operation unless it becomes destratified during backwashing. The particle density wetted in water, which is defined as the mass of solid GAC plus the mass of water required to fill the internal pores per unit volume of particle, determines the extent of fluidization and expansion of a given size particle during backwash. The particle hardness or abrasion number of GAC is a measure of the resistance to particle degradation in terms of the amount of attrition during the agitation of a GAC mixture.

Common GAC sizes are 12x40 and 8x30 US. standard mesh, which range in diameter from 1.68 to 0.42 mm and from 2.38 to 0.59 mm respectively. The apparent density of GAC ranges from 350 to 500 kg/m^3. The bed density backwashed drained ranges from 320 to 420 kg/m^3. The particle density wetted in water ranges from 1300 to 1500 kg/m^3 (Snoeyink 1990).

The mass transfer zone, termed as **MTZ,** is the region of an adsorption column in which adsorption occurs. The length of MTZ, $\mathbf{L}_{mtz}$, depends on the rate of adsorption and the solution flow rate. Factors that cause a higher rate of adsorption, such as a smaller carbon particle size, higher temperature, a larger diffusion coefficient of adsorbate, and greater strength of adsorption of adsorbate, will reduce L_{mtz}.

The breakthrough concentration for a column, $\mathbf{C_b}$, is defined as the maximum acceptable effluent concentration. The critical depth of a column, $\mathbf{L_c}$, is the depth that governs to the immediate appearance of an effluent concentration equal to C_b when the column is started up. For the situation in which C_b is defined as the minimum detectable concentration, L_c is equal to L_{mtz}.

Empty-bed contact time, **EBCT**, is the ratio of the tank volume occupied by the activated carbon divided by the volumetric flow rate. The minimum empty-bed contact time, $\mathbf{EBCT_{min}}$, can be calculated from the following equation (in which Q is the flow rate and A is the area of the column):

$$EBCT_{\min} = \frac{L_c}{Q/A}$$

Eq. 3.3 Minimum Empty-Bed Contact Time

Several tools, including pilot columns, small-scale columns, mass transfer models, and adsorption isotherms, have been developed to predict the performance of a full-scale GAC system. Pilot columns have the same flow rate, type of carbon, and influent water as the full-scale contactor that is to be designed. The minimum column-diameter to particle-size ratio should be 50 to avoid channeling and wall effects (Crittenden 1991). The internal diameter (**ID**) of pilot columns, therefore, ranges from 25 to 150 mm

(Oxenford and Lykins Jr. 1991). Pilot column studies provide the most accurate information about the effectiveness, $EBCT_{min}$, and service time of GAC columns for achieving the treatment goals. However, these studies are time-consuming and relatively expensive.

Small-scale columns, use small columnn sizes and small GAC particles in order to shorten the operation time and to reduce the cost. The GAC used in these columns is crushed until it is an appropriate size for the small columns. Small-scale columns can be used to assess both the adsorption capacity and kinetics. However, they cannot be used to predict the impact of background organic matter.

Several mathematical models of the adsorption process are available (Weber and Smith 1987). These models have led to a better understanding of the adsorption process, to determine high-priority areas for future study, and to determine cost-effective ways to design and operate activated carbon systems. The recent models, however, do not permit the making of long-term and accurate predictions of trace compound removal from a mixture of adsorbable organics. The major advantage of these models is that they require a small amount of pilot or small-scale data for designing a full-scale system.

Adsorption isotherms have extensively been used to describe adsorption behavior and to estimate the adsorption capacity of activated carbon for removing organic compounds from water. Isotherms can be used, directly or by incorporating them into kinetic models, to select the best carbon among the alternatives, to estimate the life of carbon in an adsorber, and to examine the remaining adsorption capacity of a carbon adsorber. It should be recognized, however, that the competitive effects of background organics in isotherm tests are not the same as in column studies.

Traditionally, GAC has been used as an adsorber medium arranged after sand filters for removing taste and odor and other trace organics. For this purpose, GAC postfilter-adsorbers are typically operated at 2.5 - 5.0 gpm/sq ft (Hager and Flentje 1965). GAC postfilter-adsorbers have greater flexibility in using medium particle sizes because head loss and filtration considerations are no longer constrains affecting size or uniformity coefficient; are backwashed less frequently resulting in a better stratification and fewer carbon losses; can be designed for easy replacement of carbon, utilize more of the adsorptive capacity of the carbon, may provide an additional barrier against microbial penetration, remove a larger amount of organics, and are more compatible with other processes such as ozone (Graese et al. 1987).

In contrast to that, GAC has also been employed as a filter-adsorber medium for removing particles as well as dissolved organic matter. Filter-adsorbers can be constructed simply by replacing all or a portion of the existing granular media in filters with GAC, and these are usually operated at 1.6 - 2.0 gpm/sq ft (Hyde et al. 1987). GAC filter-adsorbers have lower capital costs than postfilter-adsorbers; may be limited to short EBCTs (espicially sand replacement systems); may incur greater carbon losses because more frequent backwashing is required; and may have greater operational costs because less organic matter can be adsorbed per unit weight of carbon (Graese et al. 1987).

The life of GAC beds ranges from 0.5 to 5.0 years, depends upon the appearance frequency and intensity of taste and odor compounds, the presence of organic competitors, and the acceptable levels of all the compounds in the treated water. Intense earthy-musty odors caused by actinomycetes and algae at Mt. Clemens in Michigan, for example, were effectively controled by GAC filtration, with GAC life ranging from three to four years. At Granite City in Illinois, musty-moldy odors attributed to actinomycetes and algae metabolites were controled through GAC filtration, with GAC bed life up to three years. The GAC employed as postfilter-adsorber medium in Regina Saskatchwan must be regerated after one taste and odor season, which is typically five months long. This filter-adsorber system, which has an EBCT of 20 min, is used to control sour, musty, grassy, and septic odors from algal blooms that occur at threshold odor numbers (TONs) as high as 50 (Graese et al. 1987). Case history information is, therefore, difficult to adopt at different utilities.

The higher cost for GAC may be offset by selecting a proper empty bed contact time (EBCT) that promotes the best efficiency, i.e. the maximum volume treated for a given treatment objective (Crittenden et al. 1987). The specific volume treated will increase as the EBCT increases. Correspondingly, the carbon usage rate will decrease. For this reason, the actual EBCT must be significantly greater than the critical EBCT.

For a given EBCT, arranging GAC beds in parallel, series, or a pulsed system can also reduce the carbon usage rate from that which is possible with a single-stage contactor (Roberts and Summers 1982, Hand et al. 1984, Crittenden et al. 1987, Hand et al. 1989, and Soeyink 1990). A lower carbon usage rate results in a lower operating cost (in terms of replacement or regeneration cost). However, a larger contactor size requires a greater capital cost. Accordingly, a trade-off between capital and operating costs is necessary to determine the optimum EBCT.

Carbon Usage Rate. The minimum carbon dosage can be estimated if the isotherm capacity and the treatment objective are known. The following equations were developed by Crittenden et al. (1987). The minimum PAC dosage, termed as $\mathbf{D_{PAC}}$, can be estimated from Eq. 3.4.

$$D_{PAC} = (C_0 - C_{t0}) / (K C_{t0}^{1/n})$$

Eq. 3.4 Minimum PAC Dosage

The minimum GAC dosage $\mathbf{D_{GAC}}$ and the maximum number of bed volumes fed $\mathbf{BVF_{max}}$ are given by the following equations.

$$D_{GAC} = (C_0 - C_{t0}) / (K C_0^{1/n})$$

Eq. 3.5 Minimum GAC Dosage

$$BVF_{\max} = d_b / D_{GAC}$$

Eq. 3.6 Maximum Bed Volumes Fed

In these equations :

C_0 = initial or influent concentration ($M/L^{3,\text{ e.g mg/L}}$).

C_{to} = aqueous-phase concentration of the treatment objective ($M/L^{3,\text{ e.g. mg/L}}$).

d_b = bed density-backwashed-drained of the GAC ($M/L^{3,\text{ e.g. mg/L}}$).

Equation 3.4 assumes that the equilibrium surface concentration for PAC is evaluated at the treatment objective. Equation 3.5 and 3.6 assume that the effluent concentration continually meets the treatment objective and that the GAC leaving the process is in equilibrium with the influent concentration. By comparing the carbon dosages for GAC and PAC, it can be demonstrated that the GAC usage rate is far less than the PAC usage rate.

Chapter 4

EXPERIMENTAL MATERIALS AND METHODS

4.2 MATERIALS

Raw water. Samples of Lake Stormon water were taken from the existing intake station. The water was collected in 5-gal plastic jars and transported to the laboratory at the University of Manitoba. One of these jars was stored at 4^0C and the others were stored at room temperature (approximately 24^0C) until the water was used, usually less than four weeks. Data of the raw water quality ere presented in Tables 5.1.a and 5.1.b.

Reagents. Aluminum sulfate (alum), coagulant-aid, and PAC used in these experiments were the same as those employed by the water treatment plant. As specified by the supplier (Border Chemical Co. Ltd., Transcona, MB.), the liquid alum contained 650 grams dry aluminum sulfate-per-liter. The alum stock solution of 10 mg/L was prepared by diluting the liquid alum with distilled deionized water (**DDW**). The working solution of 0.1 mg/L of coagulant-aid was prepared (less than 2 hours before application) by dissolving the powdered coagulant-aid in DDW. The working PAC slurry of 1.0 mg/L was prepared by adding the PAC into DDW.

The potassium permanganate stock solution was prepared by dissolving the crystal permanganate (produced by Fisher Chemical Co., Fair Lawn,NY.) in DDW. The solution was standardized by titration of known amounts of sodium oxalate, as described in Standard Methods (1989).

Rapid sand filter column. Rapid filtration was condocted through a 5.1-cm ID glass column containing 76.2-cm of filter medium and 5.0-cm of supporting medium. The filter medium was a silica sand with an effective size of 0.35 mm, a specific gravity of 2.68 g/L, and a void ratio in packed-bed of 0.42. The supporting medium was a silica gravel with a minimum size of 0.85 mm, a specific gravity of 2.68 g/L, and a void ratio in packed-bed of 0.42. The media were supported by 2 overlapping fiberglass screens. The schematic of the sand filter column is shown in Figure 4.1.

An adjustable peristaltic pump was employed to provide an influent flow rate of 210 mL/min (or 2.5 gpm/sq ft). The filtration rate was maintained by regulating the effluent port to keep the water surface in the column at a constant level. The first 1400 mL of filtered water was discarded, and so was the last 1400 mL of filtered water. Before filtration of each batch, the filter was backwashed with tap water for about 10 minutes at 30-percent expansion.

GAC column. For this study, a 9.5-cm ID glass column packed with 1200 mL of GAC medium (17 cm depth) was utilized (Figure 4.2). The properties of the GAC (American Norit Co. Inc.) are summarized in Table 4.1. Before instalation, the GAC was prewetted in DDW for 24 hours. A flow rate of 600 mL/min (or 2.0 gpm/sq ft) was maintained by adjusting the effluent port to keep the water surface in the column steady at a desired level. The EBCT of this pilot column was approximately 2.0 min. The first 600 mL of effluent was discarded, and so was the last 600 mL of effluent. Before application of each batch, the column was backwashed with tap water for 5 minutes at 30-percent expansion to break-up the occurrence of unexpected channels.

Table 4.1 GAC Media Properties

PROPERTY	QUANTITY
Apparent density, g/mL	0.39
Bed density-backwashed-drained, g/mL	0.39
Particle density wetted in water, g/mL	1.40
Total pore volume, mL/g	7.0
Total surface area (N_2 BET method), m^2/g	625
Iodine Number	600
Iodine Number-min	500
Molasses Number	350
Mean pore radius, nm	2.9
Tannin value, ppm max	280
Voids in packed bed, %	50
Sieve analysis (US Sieve Series)	
larger than # 8 - max %	8
smaller than #20 - max %	5
Effective Size, mm	0.8-1.0
Uniformity Coefficient (max)	1.9
Moisture content, %	8
Abrasion % retention - min (Stirring Abrasion Test)	70

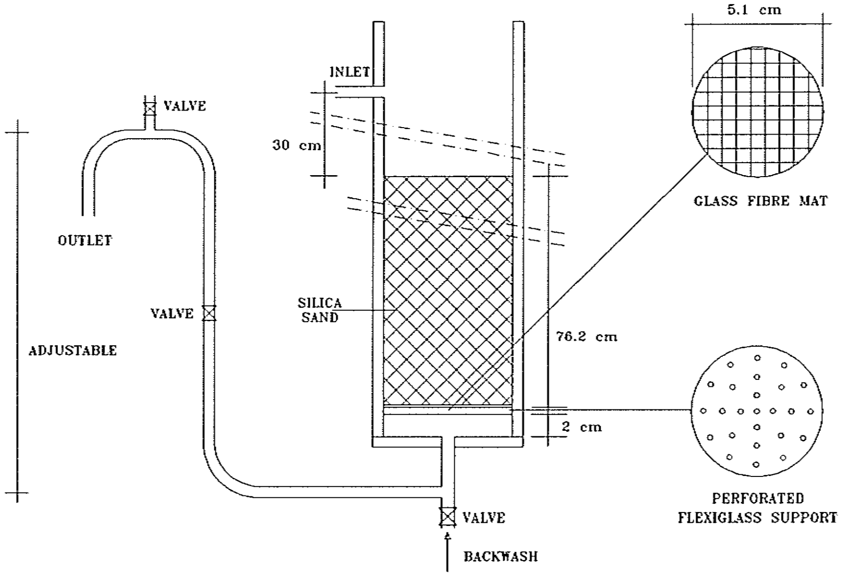


Figure 4.1 Sand Filter Column

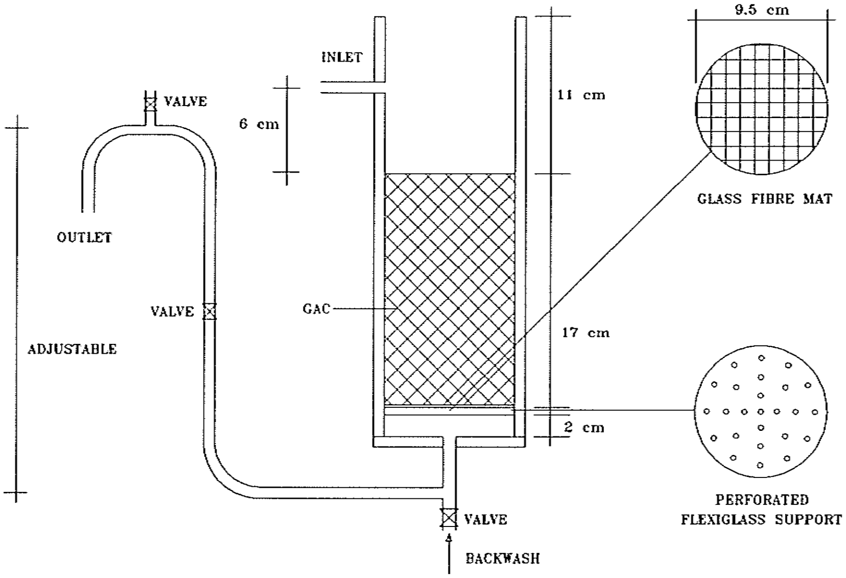


Figure 4.2 GAC Pilot Column

4.2 ANALYTICAL TECHNIQUES

Threshold Odor Number. Odor intensity of the odor-bearing water was measured using the threshold odor method, as summarized in section 3.2.1 of this report (tken from section 207 of the seventeenth edition of Standard Methods (1989). The measurements were conducted at room temperature (approximately 24^{0}C). During this study, 300-ml (instead of 500-mL) glass stoppered flasks were used to prepared the samples for odor measurements. Distilled deionized water (DDW) was employed as the odor-free water. Prior to sniffing tests, the samples were preheated to a temperature of 60^{0}C on an adjustable hot-plate. The threshold odor number (TON) values were calculated from Eq. 3.1.

The odorless samples were then tasted to evaluate their overall sensations (flavors). For these, the temperature of the samples were carried to 40^{0}C or less.

Most of the measurements were established by the author as the single tester. To improve the results, the acuity of the single tester was occasionally assessed by the other testers. In addition, a panel of four members was developed at the International Peace Garden to evaluate the acceptability of the treated water produced by the proposed treatment.

Total Organic Carbon. Total organic carbon (TOC) of the water samples was measured using a Dorhman DC-80 carbon analyzer as described in section 5310 C of the seventeenth edition of Standard Methods (1989). First of all, the machine's instuctions were followed for power up, reagent production, and calibration. The water samples were automatically injected into the machine after acidification to pH 2. For each water sample, two or more tests were performed. The TOC for this water sample was calculated as the average of the individual TOC values by excluding the exterme values.

Alkalinity. The alkalinity of the water samples was measured by titrating to neutralize acid destroying ions, as described in section 2320 B of the seventeenth edition of Standard Methods (1989). Fifty milliliter of each water sample was titrated with sulfuric aicd (0.02 N H_2SO_4) until the pH dropped to 8.3. This titrant volume, termed as P, was related to the phenolphthalein alkalinity. The titration continued until the pH was reduced to 4.5. The total titrant volume (including P), symbolized as T, was associated with the total alkalinity. Table 4.2 and equation 4.1 were used to differentiate and calculate the different forms of alkalinity.

Table 4.2 Alkalinity relationships (Standard Methods 1989)

RESULT OF TITRATION	HYDROXIDE ALKALINITY AS $CaCO_3$	CARBONATE ALKALINITY AS $CaCO_3$	BICARBONATE CONCENTRATION AS $CaCO_3$
P = 0	0	0	T
P < 1/2 T	0	2P	T - 2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P - T	2(T - P)	0
P = T	T	0	0

$$Alklinity, mgCaCO_3/L = \frac{.02N \times 50{,}000\ mg/mole \times mL\ of\ titrant}{mL\ of\ sample}$$

Eq. 4.1 Alkalinity as $CaCO_3$

pH. The pH of the raw and treated waters were measured by using a glass electrode probe as described in section 4500-H B of the seventeenth edition of Standard Methods (1989). The pH meter was calibrated at pH 7 and 10 using buffer solution prepared by Fisher Scientific, prior to pH measurement.

Apparent Color. The apparent color of the raw and treated waters was measured using a Hellige Aqua Tester. The principle of this method is described in section 2120 B of the seventeenth edition of Standard Methods (1989). The Aqua Tester is equiped with a color disk which was factory calibrated againts platinum cobalt standard. Two nessler tubes were filled, one with the DDW and the other one with the sample water. These tubes were than placed in the tester. The shade of the sample tube was matched to the DDW tube by rotating the color disk. Finally, the color unit appeared in the disk was recorded.

Turbidity. The turbidity of the raw and treated waters was measured using a nephelometer (model DRT15B) made by HF Instruments. The results were expressed in nephelometric turbidity units (**NTU**), as described in section 2130 B of the seventeenth edition of Standards Methods (1989). Before each test, the nephelometer was calibrated using a 0.1 NTU standard. The measurements were performed by filling the test tube with samplewater and placing it in the sample hole of the nephelometer.

PAC Adsorption Isotherm. The PAC adsorption isotherm study was performed to determine the minimum PAC dosage (consider section 3.3.4) without reaching the equilibrium condition. The adsorption time was 15 min, which was the same as the existing adsorption time provided in the plant. The treatment objective of this study was the production of a treated water with a TON = 1.

4.3 EXPERIMENTAL PROCEDURE

Microscopic examination. The purpose of this study was to find out the kinds of microorganisms responsible for the occurrance of taste and odor problems. Approximately 200 mL of the raw water contained in a 500-mL glass jar was being exposed to sun-light at room temperature for 7-14 days. A drop of the settled biomass was drawn from the bottom of the jar and placed under the 40X objective of a microscope. At a total magnification of 400 power, Anacystis, a blue-green alga, was observed to be predominant.

Preliminary examination. A series of jar-tests providing a reasonable simulation of the full-scale plant was conducted to identify the optimum conditions for the removal of color, turbidity, and TOC by alum, coagulant-aid, and permanganate. Since the existing treatment relies on coagulation, this experiment began with a study of the optimum coagulant dosage.

Several dosages of alum (60, 80, 100,120, and 150 mg/L) were investigated under a typical jar-testing procedures. The samples were mixed at 80 rpm for one minute, flocculated at 40 rpm for 17 min, and settled by standing for 30 min. One half milligram-per-liter of coagulant-aid was added at the beginning of the flocculation process. The supernatants were filtered through prewashed glass-fibre filter. The filtered effluents were then subjected to the measurements of pH, alkalinity, color, tubidity, and TOC. The results are presented in Table 5.2.

To determine the optimum dosage of coagulant-aid, three different dosages of coagulant-aid (0.25, 0.50, 1.00 mg/L) were surveyed under the typical jar-testing procedures. Prior to rapid mixing at 80 rpm, two dosages of alum (120 and 150 mg/L) were provided. The pH, alkalinity, color, turbidity, and TOC of the filtered effluents were then measured. The results are presented in Tables 5.3.a and 5.3.b.

Three different dosages of standardized potassium permanganate (0.5, 1.0, and 2.0 mg/L) and two different reaction times (30 and 60 min) were provided to study the effects of permanganate oxidation. To establish completely-mixed-batch experiments, the samples were agitated at 80 rpm. Prior to filtration with glass-fiber filter, the permanganated waters were treated with the optimized dosages of alum and coagulant-aid (150 mg/L and 0.5 mg/L respectively) under the typical jar-testing procedures. The data resulted from analytical measurements are summarized in Tables 5.4.a and 5.4.b.

PAC study. In this study, the PAC was mixed with the supernatant which was obtained from the optimized permanganation and coagulation pretreatments. Proper amounts of PAC were added to separate jars containing the same amount of the supernatant to make PAC dosages of 10, 20, 30, and 40 mg/L. These samples were then agitated at 40 rpm for 15 min. After sedimentation (for 30 min), the PAC supernatants were pumped into the sand filter. The chemical quality of the effluents, supernatants, and raw water are presented in Tables 5.5.a and 5.5.b. The data in Table 5.5.b were then used for adsorption isotherm study. This study simulates the most profitable point of PAC application.

GAC study. Three parallel trains were run to provide coagulation, permanganation-coagulation, and permanganation-coagulation-PAC adsorption pretreatments. Permanganate, alum, and coagulant-aid were dosed in the same way as described earlier, while fifteen milligram per liter of PAC was dosed into the flocculation process (two minutes after coagulant-aid addition). The third train, therefore, provided reasonable simulation of the existing treatment processes.

The filtrate produced by the third train was subjected to a GAC study (Figure 4.3). First of all, the filtrate was passed through the GAC column to produce a 2-min-EBCT effluent. One liter of this effluent was collected in a 1-L glass stoppered bottle for quality measurements, while the remaining was introduced to the GAC column to produce a 4-min-EBCT effluent. The 6, 8, and 10-min-EBCT effluents were produced using the same procedures as described above. The results of the analytical measurements are summarized in Tables 5.7.a, 5.7.b, 5.8.a, and 5.8.b.

In subsequent tests, the filter effluent from the first train was subjected to the same GAC study. The purpose of this study is to examine the possibility of excluding permanganate and PAC from the treatment train. The results are given in Tables 5.9.a, 5.9.b, 5.10, and 5.11.

Field study. An experiment using fresh raw water was established at the International Peace Garden water treatment plant on August 15, 1991. Three lab-scale treatment trains providing permangation-coagulation, coagulation-PAC adsorption, and coagulation-GAC adsorption were run simultaneously under the optimized conditions. Two hundred milliliter of the effluents and standard odor-free water (DDW) were prepared in separate 300-mL glass-stopered flasks (two samples for each effluent). The samples were then heated to a temperature of 60°C and presented to a panel of four members for sniffing tests. The results are summarized in Table 5.12.

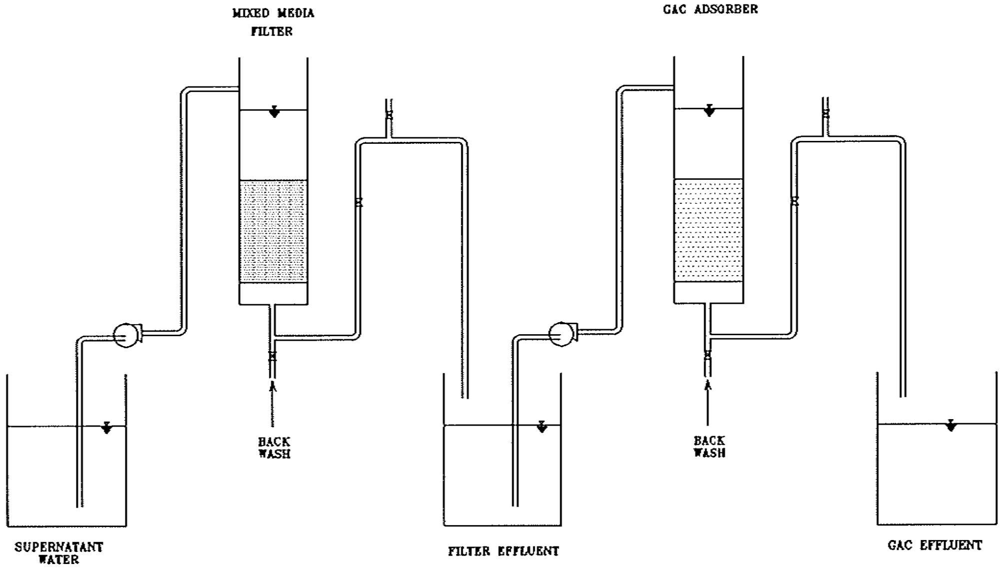


Figure 4.3 Experimental Treatment Scheme

Chapter 5

EXPERIMENTAL RESULTS

The raw water quality. The raw water quality measured during this study is summarized in Table 5.1.a and 5.1.b. The typical values of the raw water quality were pH-6.8 to 8.3, alkalinity-162 to 184 mg $CaCO_3$/L, color-20 to 100 CU, turbidity-1.2 to 9.1 NTU, TOC-13.9 to 25.6 mg/L, and TON-12 to 24. The TON values were not measured during the preliminary study.

The optimized dosage of alum. The acceptable effluent color (< 5 CU) and turbidity (< 1.0 NTU) was achieved by the alum dosage of 120 and 150 mg/L (Table 5.2). The TOC removal increased as the alum dosage increased; however, an alum dosage greater than 150 mg/L will significantly reduce the buffering capacity (alkalinity) of the water to an undesirable level. Accordingly, the optimized dosage of alum in the presence of 0.5 mg coagulant-aid-per-liter was 150 mg/L.

The optimized dosage of coagulant-aid. Tables 5.3.a and 5.3.b show the treated water quality produced by the acceptable dosages of alum (120 and 150 mg/L) in conjuction with three different dosages of coagulant-aid (0.25, 0.5, and 1.0 mg/L). In general, the coagulant-aid was found to has insignificant effects on the water quality parameters;

however a greater dosage of coagulant-aid was found to improve the formation of flocs. The medium dosage of coagulant-aid (0.5 mg/L) was, therefore, selected as the optimum dosage.

The optimized dosage and reaction time of permanganate. The data in tables 5.4.a and 5.4.b were obtained by treating the permanganated water with 150 mg alum-per-liter and 0.5 mg coagulant-aid-per-liter. The data indicate that the applied dosages and reaction times produced comparable results in terms of color, turbidity, and TOC removal. However, permangante dosage of 1.0 mg/L and reaction time of 30 min were selected for further experiments since these values represent the existing conditions.

PAC adsorption isotherm. The adsorption isotherm data given in Table 5.6 and graphed in Figure 5.1 were calculated from the data in Table 5.5.b. A best fit line was drawn through the points on the graph. This gives a slope (1/n) of 0.1745 and an adsorption capacity (K) of 320. The minimum PAC dosage which is required to reduce the TON of the permanganated-coagulated supernatant from 17 to 1 is 50 mg/L (calculated from Eq. 3.4).

Minimum EBCT of the GAC. To determine the minimum EBCT, the effluent quality produced by the GAC column was examined with respect to odor removal in terms of TON. The data which are given in Table 5.8.b and graphed in Figure 5.2 indicate that an EBCT of 10 min was required to completely remove the odor of the influent water.

The data in Table 5.7.b, which were obtained from the other run, indicates the same minimum EBCT. When the TON of the influent was somewhat lower (Table 5.9.b), an EBCT of 2 min was adequate to produce odorless water. The 10-min-EBCT was, however, assigned to be the minimum EBCT, so as to justify different applied-water quality.

Table 5.1.a Raw water quality (pH, alkalinity, and color)

DATE OF SAMPLING	DATE OF MEASUREMENT	pH	ALKALINITY mg $CaCO_3$/L	COLOR CU
190691	200691	8.3	184	30
	210691	8.2	172	25
	240691	8.2	172	40
	250691	8.2	162	20
	020791	7.7	166	20
080791	170791	7.6	162	100
	180791	7.8	168	100
	230791	7.8	172	100
	310791	6.8	166	20
	060891	7.2	162	20
150891	190891	8.2	172	50
	220891	8.0	170	50
	260891	7.8	170	30

Table 5.1.b Raw water quality (turbidity, TOC, and TON)

DATE OF SAMPLING	DATE OF MEASUREMENT	TURBIDITY NTU	TOC mg/L	TON
190691	200691	9.1	25.6	
	210691	7.4	19.5	
	240691	5.2	19.8	
	250691	5.8	17.4	
	020791	2.1	16.8	
080791	170791	2.8	23.9	
	180791	3.0	14.4	
	230791	2.0	16.5	24
	310791	1.2	13.9	17
	060891	1.2	14.5	17
150891	190891	6.7	18.0	12
	220891	5.1	16.4	12
	260891	4.3	16.4	12

Table 5.2 Optimizing the alum dosage (0.5 mg/L of coagulant-aid was added at the begining of the flocculation process)

Parameter	Raw Water	Alum 60 mg/L	Alum 80 mg/L	Alum 100 mg/L	Alum 120 mg/L	Alum 150 mg/L
pH	8.2	7.2	7.1	7.0	6.9	6.8
Alkalinity, $mgCaCO_3/L$	172	138	128	118	108	94
Color, CU	40	20	20	10	< 5	< 5
Turbidity, NTU	5.2	1.3	1.1	1.0	0.5	0.5
TOC, mg/L	19.8	18.5	17.5	17.1	16.2	15.3

Table 5.3.a Optimizing the coagulant-aid dosage (120 mg/L of alum was provided prior to rapid mixing process)

Parameter	Raw Water	Coag.-aid 0.25 mg/L	Coag.-aid 0.5 mg/L	Coag.-aid 1.0 mg/L
pH	7.7	6.9	6.8	6.8
Alkalinity, $mgCaCO_3/L$	166	102	96	94
Color, CU	20	< 5	< 5	< 5
Turbidity, NTU	2.1	0.5	0.3	0.4
TOC, mg/L	16.8	11.1	11.2	11.5

Table 5.3.b Optimizing the coagulant-aid dosage (150 mg/L of alum was provided prior to rapid mixing process)

Parameter	Raw Water	Coag.-aid 0.25 mg/L	Coag.-aid 0.5 mg/L	Coag.-aid 1.0 mg/L
pH	7.7	6.6	6.6	6.6
Alkalinity, $mgCaCO_3/L$	166	85	85	86
Color, CU	20	< 5	< 5	< 5
Turbidity, NTU	2.1	0.5	0.4	0.3
TOC, mg/L	16.8	9.9	10.0	10.1

Table 5.4.a Optimizing the permanganate dosage with a reaction time of 30 min (the permanganated water was treated with 150 mg alum/L and 0.5 mg coagulant-aid/L)

Parameter	Raw Water	$KMnO_4$ 0.5 mg/L	$KMnO_4$ 1.0 mg/L	$KMnO_4$ 2.0 mg/L
pH	7.6	6.4	6.5	6.5
Alkalinity, $mgCaCO_3/L$	162	74	78	76
Color, CU	100	< 5	< 5	< 5
Turbidity, NTU	2.8	0.3	0.4	0.6
TOC, mg/L	23.9	14.6	14.5	14.0

Table 5.4.b Optimizing the permanganate dosage with a reaction time of 60 min (the permanganated water was treated with 150 mg alum/L and 0.5 mg coagulant-aid/L)

Parameter	Raw Water	$KMnO_4$ 0.5 mg/L	$KMnO_4$ 1.0 mg/L	$KMnO_4$ 2.0 mg/L
pH	7.6	6.5	6.5	6.6
Alkalinity, $mgCaCO_3/L$	162	76	82	82
Color, CU	100	< 5	< 5	< 5
Turbidity, NTU	2.8	0.4	0.5	0.5
TOC, mg/L	23.9	14.3	14.0	14.0

Table 5.5.a Chemical quality of the raw water and the finished water resulting from coagulation and permanganation-coagulation processes.

Parameter	Raw Water	Alum + Coag.-aid	$KMnO_4$ + Alum + Coag.-aid
pH	7.8	6.6	7.0
Alkalinity, $mgCaCO_3/L$	172	88	88
Color, CU	100	< 5	< 5
Turbidity, NTU	2.0	0.2	0.4
TOC, mg/L	16.5	10.4	10.4
TON	24	17	17

Note : $KMnO_4$ = 1.0 mg/L-30 min; Alum = 150 mg/L;
Coagulant-aid = 0.5 mg/L

Table 5.5.b Chemical quality of the finished water resulting from permanganation-coagulation (PAC = 0) and permanganation-coagulation-PAC adsorption processes (PAC was mixed with the supernatant resulted from permanganation-coagulation pretreatment).

Parameter	PAC 0 mg/L	PAC 10 mg/L	PAC 20 mg/L	PAC 30 mg/L	PAC 40 mg/L
pH	7.0	7.1	7.1	7.1	7.1
Alkalinity, $mgCaCO_3/L$	88	88	88	88	88
Color, CU	< 5	< 5	< 5	< 5	< 5
Turbidity, NTU	0.4	0.5	0.6	0.7	0.9
TOC, mg/L	10.4	10.0	9.9	9.8	9.6
TON	17	12	8	4	2

Note : $KMnO_4$ = 1.0 mg/L-30 min; Alum = 150 mg/L; Coagulant-aid = 0.5 mg/L

Table 5.6 PAC adsorption isotherm using TON (taken from Table 5.5.b) with the Freundlich model.

PAC Dosage (m) mg/L	C_e (Final) TON	$x = (C_0 - C_e)$ TON	$q_e = x/m$ TON L/g
0	17	0	
10	12	5	500
20	8	9	450
30	4	13	433
40	2	15	375

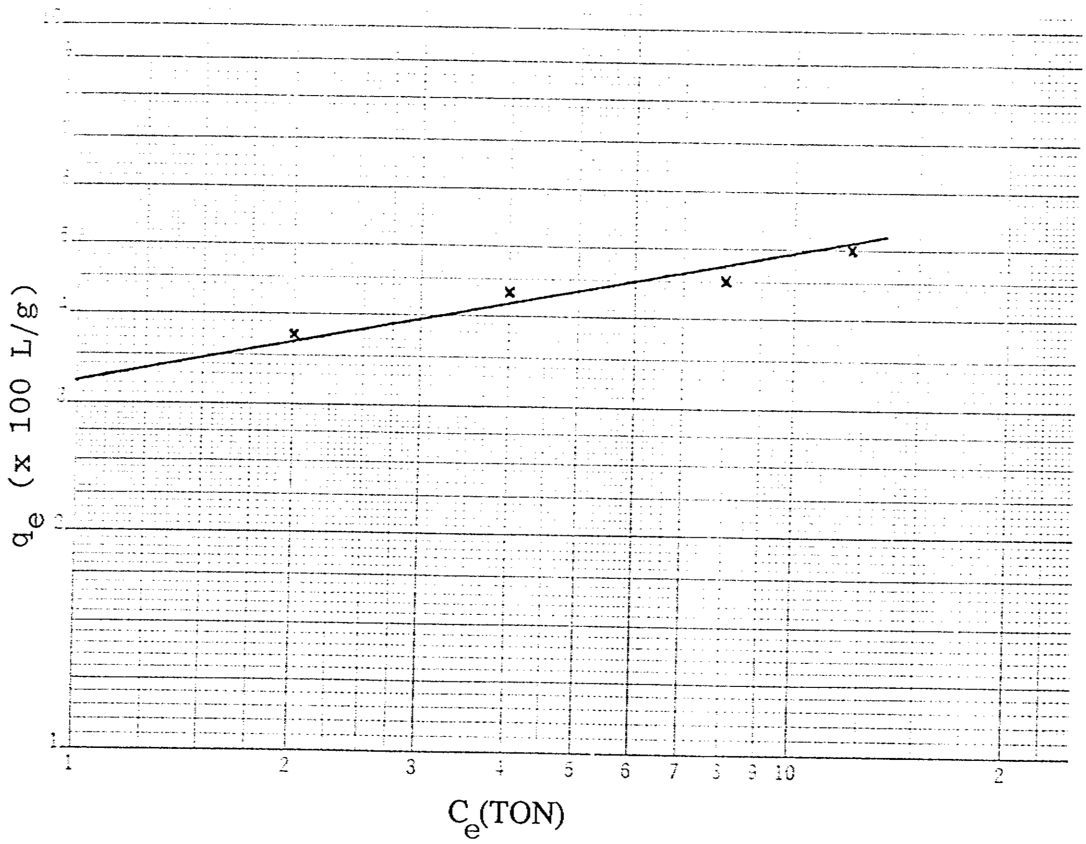


Figure 5.1 PAC isotherm

Table 5.7.a Chemical quality of the raw water and the finished water resulting from coagulation, permanganation-coagulation, permanganation-coagulation-PAC adsorption processes (PAC was introduced into the flocculation process as done in the existing treatment)

Parameter	Raw Water	Alum + Coag.-aid	$KMnO_4$ + Alum + Coag.-aid	$KMnO_4$ + Alum + Coag.-aid + PAC
pH	6.8	6.6	6.9	7.2
Alkalinity, $mgCaCO_3/L$	166	90	90	94
Color, CU	20	< 5	20	10
Turbidity, NTU	1.2	0.5	1.4	1.4
TOC, mg/L	13.9	9.1	8.8	8.3
TON	17	12	12	12

Note : $KMnO_4$ = 1.0 mg/L-30 min, Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L,
PAC = 15 mg/L

Table 5.7.b Chemical quality of the finished water resulting from permanganation-coagulation-PAC adsorption (EBCT = 0) and permanganation-coagulation-PAC adsorption-GAC adsorption (PAC was introduced into the flocculation process as done in the existung treatment)

Parameter	EBCT 0 min	EBCT 6 min	EBCT 8 min	EBCT 10 min
pH	7.2	7.5	7.5	7.6
Alkalinity, $mgCaCO_3/L$	94	90	80	70
Color, CU	10	< 5	< 5	< 5
Turbidity, NTU	1.4	1.4	1.3	1.2
TOC, mg/L	8.3	1.5	1.4	1.4
TON	12	1.4	1.0	0

Note : $KMnO_4$ = 1.0 mg/L-30 min, Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L
PAC = 15 mg/L

Table 5.8.a Chemical quality of the raw water and the finished water resulting from coagulation, permanganation-coagulation, and permanganation-coagulation-PAC adsorption processes (PAC was introduced into the flocculation process as done in the existing treatment)

Parameter	Raw Water	Alum + Coag.-aid	$KMnO_4$ + Alum + Coag.-aid	$KMnO_4$ + Alum + Coag.-aid + PAC
pH	7.2	6.6	6.8	7.0
Alkalinity, $mgCaCO_3/L$	162	90	90	90
Color, CU	20	< 5	10	5
Turbidity, NTU	1.2	0.2	0.5	0.6
TOC, mg/L	14.5	9.6	9.5	9.7
TON	17	12	12	12

Note : $KMnO_4$ = 1.0 mg/L-30 min, Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L
PAC = 15 mg/L

Table 5.8.b Chemical quality of the finished water resulting from permanganation-coagulation-PAC adsorption (EBCT = 0) and permanganation-coagulation-PAC adsorption-GAC adsorption processes (PAC was introduced into the flocculation process as done in the existing treatment)

Parameter	EBCT 0 min	EBCT 2 min	EBCT 4 min	EBCT 6 min	EBCT 8 min	EBCT 10 min
pH	7.0	7.2	7.2	7.4	7.4	7.4
Alkalinity,$mgCaCO_3/L$	90	90	90	90	82	72
Color, CU	5	< 5	< 5	< 5	< 5	< 5
Turbidity, NTU	0.6	0.7	0.7	0.8	0.9	0.9
TOC, mg/L	9.7	3.0	2.7	2.4	2.2	2.0
TON	12	8	6	4	1.4	0

Note : $KMnO_4$ = 1.0 mg/L-30 min, Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L
PAC = 15 mg/L

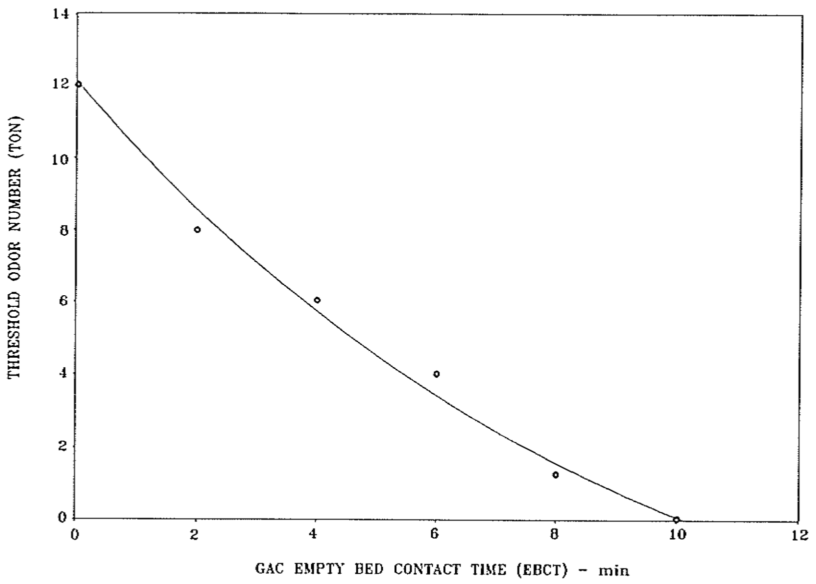


Figure 5.2 GAC Empty Bed Contact Time (EBCT)

Table 5.9.a Chemical quality of the raw water and the finished water resulting from permanganation-coagulation, permanganation-coagulation-PAC adsorption, and coagulation processes (PAC was introduced into the flocculation process as done in the existing treatment)

Parameter	Raw Water	$KMnO_4$ + Alum + Coag.-aid	$KMnO_4$ + Alum + Coag.-aid + PAC	Alum + Coag.-aid
pH	8.2	7.0	7.0	7.0
Alkalinity, $mgCaCO_3/L$	172	102	102	102
Color, CU	50	10	< 5	< 5
Turbidity, NTU	6.7	0.8	0.4	0.4
TOC, mg/L	18.0	10.5	10.2	10.9
TON	12	4	4	4

Note : $KMnO_4$ = 1.0 mg/L-30 min, Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L
PAC = 15 mg/L

Table 5.9.b Chemical quality of the finished water resulting from coagulation (EBCT = 0) and coagulation-GAC adsorption processes.

Parameter	EBCT 0 min	EBCT 2 min	EBCT 4 min	EBCT 6 min	EBCT 8 min	EBCT 10 min
pH	7.0	7.2	7.2	7.2	7.4	7.4
Alkalinity,$mgCaCO_3/L$	102	102	98	82	78	74
Color, CU	< 5	< 5	< 5	< 5	< 5	< 5
Turbidity, NTU	0.4	0.4	0.6	0.6	0.7	0.8
TOC, mg/L	10.9	3.0	2.6	2.3	2.2	2.2
TON	4	0	0	0	0	0

Note : Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L

Table 5.10 Chemical quality of the raw water and the finished water resulting from coagulation and coagulation-GAC adsorption

Parameter	Raw Water	Alum + Coag.-aid	Alum + Coag.-aid + EBCT 10 min
pH	8.0	7.2	7.6
Alkalinity, mgCaCO$_3$/L	170	103	82
Color, CU	50	5	< 5
Turbidity, NTU	5.1	0.5	0.9
TOC, mg/L	16.4	10.5	2.1
TON	12	4	0

Note : Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L

Table 5.11 Chemical quality of the raw water and the finished water resulting from coagulation and coagulation-GAC adsorption

Parameter	Raw Water	Alum + Coag.-aid	Alum + Coag.-aid + EBCT 10 min
pH	7.8	6.9	7.6
Alkalinity, mgCaCO$_3$/L	170	100	78
Color, CU	30	5	< 5
Turbidity, NTU	4.3	0.6	0.9
TOC, mg/L	16.4	9.8	2.9
TON	12	4	0

Note : Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L

Table 5.12 Field study assesment using fresh-raw water

Sample water	Panelist 1 discription	Panelist 2 discription	Panelist 3 discription	Panelist 4 discription
Raw Water	earthy	earthy	earthy	earthy
$KMnO_4$-coagulation 1	earthy	earthy	earthy	earthy
2	earthy	earthy	earthy	earthy
Coagulation-PAC 1	earthy	earthy	earthy	odorless
2	earthy	earthy	earthy	odorless
Coagulation-GAC 1	odorless	odorless	odorless	odorless
2	odorless	odorless	odorless	odorless

Note : $KMnO_4$ = 1.0 mg/L-30 min, Alum = 150 mg/L, Coagulant-aid = 0.5 mg/L
PAC = 15 mg/L, GAC EBCT = 10 min

Chapter 6

DISCUSSION

The earthy odor in the Internatinal Peace Garden water may be caused by naturally-occurring organics produced by microorganisms. At a total magnification of 400 power, Anacystis was observed to be predominant. Anacystis, a planktonic blue-green alga, has long been associated with earthy-musty odor problems, although it has never been identified to produce earthy-musty smelling compounds geosmin and MIB. A substantial portion of the problem could be attributed to other micro-organisms, such as benthic algae and Actinomycetes, that were not detected during this study.

Coagulation employing alum and coagulant-aid was performed primarily to reduce the turbidity and color of the International Peace Garden water. An examination using an iron test-kit (HACH Model IR-18, 0 to 5 mg/L) showed that iron was present in negligible concentrations. The causes of the raw water color could, therefore, be organic matter, including naturally-occurring organics, dissolved plant components, and planktonic microorganisms. This might govern to the demand for a high alum dosage.

The experimental data show that coagulation significantly reduced the TON of the raw water. However, no literature, at the present, supports this evidence. Research is necessary to identify the mechanism involved and factors affecting the removal.

Coagulation is generally found to preferentially remove TOC and THMs precursors that otherwise will be remove by GAC columns. In this study, a marked removal of TOC was obtained by an alum dosage of 150 mg/L. To some extent, this additional benefit will prolong the life of GAC columns and reduce the formation of THMs.

The removability of such parameters by permanganate can be studied by comparing the data obtained from the coagulation process with those resulting from the permanganation-coagulation process. As shown in Tables 5.5.a, 5.7.a,5.8.a, and 5.9.a, permanganate oxidation appears to be ineffective in removing the taste and odor compounds as well as the TOC. This observed evidence supports the recent studies on oxidation of earthy-musty smelling compounds. Moreover, permanganate tends to increase the color and turbidity of the finished water.

To study the most advantageous condition for PAC adsorption, the PAC was mixed with the supernatant resulting from permanganation-coagulation pretreatment. This study indicated that a PAC dosage of more than 50 mg/L was required to reduce the TON of the permanganated-coagulated supernatant from 17 to 1. In fact, adding separate reactors between the existing sedimentation and filtration basins that provide a 15 min-contact time and a 30 min-settling time is nearly impossible. Moreover, this PAC application will degrade the finished water quality. The observed data indicated that PAC particles penetrated the filter medium since turbidity of the finished water increased as the PAC dosage increased.

The effect of the existing PAC dose on the water quality can be studied by comparing the data obtained from permanganation-coagulation process with those resulted from permanganation-coagulation-PAC adsorption (Tables 5.7.a, 5.8.a, and 5.9.a). The applied PAC (15 mg/L dosed into the flocculation process) removed a small amount of the TOC (less than 1.0 mg/L). The literature has indicated that the relationship between TOC and THMs precursors cannot be ignored. Moreover, the applied PAC produced an undetected odor removal.

Tables 5.7.b and 5.8.b report that an EBCT of 10 min was sufficient to completely remove the odor which remained after permanganation-coagulation-PAC adsorption pretreatment. Since permanganation and PAC adsorption were found to be ineffective in reducing the TON of the water, GAC adsorption following the existing coagulation process can be postulated to combat the occurrance of earthy-musty odor in the International Peace Garden water. This postulation was confirmed by the subsequent experiments (Tables 5.9.b, 5.10, 5.11, and 5.12).

The observed data also demonstrate the effect of EBCT on TOC of the water. The TOC of the filtered effluent decreased drastically from about 10 to 3 mg/L when it was passed through the GAC column (2-min-EBCT), although further EBCTs resulted in an insignificant TOC removal. A certain removal of THMs precursors may coincide with a high TOC removal. This side benefit confirms the postulation that GAC provides an excellent barrier againts undesirable substances.

GAC is potentially effective for reducing color, so that the dosage of alum may be cut back. This reduction will result in an increase of TOC amount that has to be removed by GAC column. In turn, it will shorten the life of the GAC bed. A trade-off between alum dosage and EBCT is, therefore, necessary to minimize the overall costs.

During this study, unexpected removal of alkalinity by GAC was observed. For an EBCT of 10 min, the alkalinity removal ranged from 19 to 27 percent. The exact mechanism is not known; however, the following information may be useful. USEPA (1973) reported that hardness and alkalinity of the influent water at Orange County pilot plant California were reduced by the GAC column. Sawyer and McCarty (1978) indicated that salts of weak acids (such as organic acids, e.g. humic acids) may contribute to the alkalinity of water. The adsorption of these salts on GAC may result in the reduction of the associated alkalinity. Randtke et al. (1981) noted that a desired buffer (usually 1 mL of 0.16 M $NaHCO_3$ per 160 mL of sample) should be added to the water sample prior to the introduction of activated carbon. This information may indicate that activated carbon will reduce the buffering capacity (alkalinity) of the water sample.

Chapter 7

CONCLUSION

GAC adsorption following the existing coagulation practice is the best available technology for controlling the occurance of the earthy-musty odor in the International Peace Garden water. The optimized dosages of alum and coagulant-aid were 150 mg/L and 0.5 mg/L respectively. The minimum EBCT of GAC adsorber was 10 min. However, the most economical condition depends on a trade-off between alum dosage and EBCT. This study also proves that permanganate and PAC can be excluded from the existing treatment process.

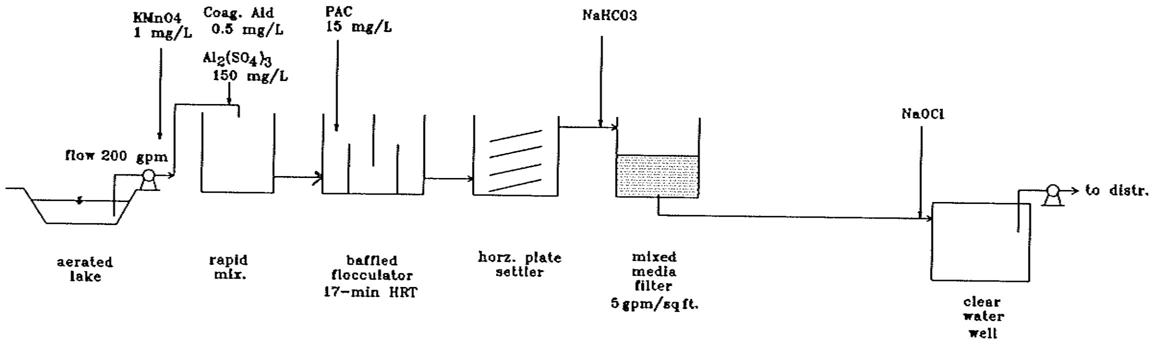
Chapter 8

RECOMMENDATIONS AND FURTHER STUDIES

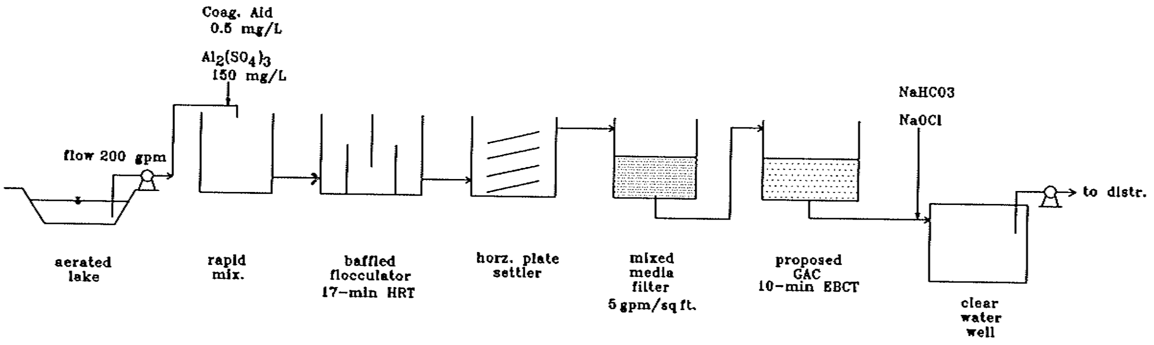
Based upon the information gathered for this thesis, I would suggest that the application of permanganate and PAC should not be continued, even when GAC adsorber has not been employed. This will reduce the chemical and operation costs. The proposed treatment scheme is presented in Figure 8.1.

This experiment used a batch method so that it only provided information about the effectiveness and minimum EBCT of the GAC column. To determine the proper EBCT that promotes the best efficiency, i.e. the least carbon usage rate or the longest life-time of the GAC, a pilot column, which is operated on the basis of continous flow is necessary. Otherwise, the econamical value of taste and odor treatment is difficult to predict.

Two importance findings of this research are that coagulation effectively removed the earthy-musty odor and the GAC column consumed a considerable amount of alkalinity. Research is required to determine the exact mechanisms and factors affecting these evidences.



(a). Exsisting Treatment Scheme



(b). Proposed Treatment Scheme

Figure 8.1 Existing and Proposed Treatment Schemes

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APPENDIX A

Table A.1 Actinomycetes that have been identified as Geosmin and MIB producers.

Actinomycetes	Products
Actinomyces biwako	Geosmin
Actinomadura sp.	MIB
Microbispora rosea	Geosmin
Nocardia sp.	Geosmin
Nocardiopsis dassonvillei	MIB
Streptomyces albidoflafus	Geosmin
Streptomyces alboniger	Geosmin
Streptomyces antibioticus	Geosmin and MIB
Streptomyces chibaensis	Geosmin and MIB
Streptomyces fradiae	Geosmin
Streptomyces fragilis	Geosmin and MIB
Streptomyces griseoflavus	Geosmin
Streptomyces griseoluteus	Geosmin and MIB
Streptomyces griseus	Geosmin and MIB
Streptomyces lavendulae	Geosmin and MIB
Streptomyces neyagawaensis	Geosmin and MIB
Streptomyces odorifer	Geosmin and MIB
Streptomyces phaeofaciens	Geosmin and MIB
Streptomyces praecox	MIB
Streptomyces prunicolor	Geosmin and MIB
Streptomyces versipellis	Geosmin and MIB
Streptomyces viridochromogenes	Geosmin
Streptomyces werraensis	Geosmin and MIB

Source : AWWARF and LdE (1987)

Table A.2 Algae-generated tastes and odors

Algae Class	Odor Description : Moderate Quantities of Algae	Odor Description : Large Quantities of Algae	Taste Description	Tactile Sensation
Cyanophyceae				
Anabaena	Grassy, musty, nasturtium	Rotten, septic, medicinal	-	-
Anabaenopsis	-	Grassy	-	-
Aphanizomenon	Grassy, musty, nasturtium	Rotten, septic, medicinal	Sweet	Dry
Cylindrospermum	Grassy	Septic	-	-
Gloeotrichia	-	Grassy	-	-
Gomphosphaeria	Grassy	Grassy	Sweet	-
Microcystis or Anacystis	Grassy, musty	Rotten, septic, medicinal	Sweet	-
Nostoc	Musty	Rotten, septic, medicinal	-	-
Oscillatoria	Grassy	Musty, spicy	-	-
Rivularia	Grassy	Musty	-	-
Chlorophyceae				
Actinastrum	-	Grassy, musty	-	-
Ankistrodesmus	-	Grassy, musty	-	-
Chara	Garlic, skunk	Musty, garlic	-	-
Chlamydomonas	Musty, Grassy	Fishy, septic medicinal	Sweet	Sicky sweet,oily
Chlorella	-	Musty	-	-
Cladophora	-	Septic	-	-
Closterium	-	Grassy	-	-
Cosmarium	-	Grassy	-	-
Dictyosphaerium	Grassy, nasturtium	Fishy	-	-
Eudorina	-	Fishy	-	-
Gloeocystis	-	Rotten, medicinal	-	-
Gonium	-	Fishy	-	-
Hydrodictyon	-	Rotten, septic	-	-
Nitella	Grassy	Grassy, rotten	Bitter	-
Pandorina	-	Fishy	-	-

Table A.2 Algae-generated tastes and odors (continued)

Algae Class	Odor Description : Moderate Quantities of Algae	Odor Description : Large Quantities of Algae	Taste Description	Tactile Sensation
Chlorophyceae				
Pediastrum	-	Grassy	-	-
Scenedesmus	-	Grassy	-	-
Spirogyra	-	Grassy	-	-
Straurastum	-	Grassy	-	-
Tribonema	-	Fishy	-	-
Ulothrix	-	Grassy	-	-
Volvox	Fishy	Fishy	-	-
Diatoms				
Asterionella	Spicy,geranium	Fishy	-	-
Cyclotella	Grassy, spicy, geranium	Fishy	-	-
Diatoma	-	Aromatic	-	-
Fragilaria	Grassy, spicy, geranium	Musty	-	-
Melosira	Grassy, spicy, geranium	Musty	-	Sickly sweet,oily
Meridion	-	Spicy	-	-
Pleurosigma	-	Fishy	-	-
Stephanodiscus	Grassy, spicy, geranium	Fishy	-	Sickly sweet,oily
Synedra	Grassy	Musty, fishy	-	Sickly sweet,oily
Tabellaria	Grassy, spicy geranium	Fishy	-	-

Table A.2 Algae-generated tastes and odors (continued)

Algae Class	Odor Description : Moderate Quantities of Algae	Odor Description : Large Quantities of Algae	Taste Description	Tactile Sensation
Chrysophyceae				
Dinobryon	Violets, fishy	Fishy	-	Sickly sweet,oily
Mallomonas	Violets	Fishy	-	-
Synura	Cucumber, rotten, medicinal, muskmelon	Fishy	Bitter	Dry, metalic, sickly sweet,oily
Uroglenopsis	Cucumber	Fishy	-	Sickly sweet,oily
Euglenophyceae				
Euglena	-	Fishy	Sweet	-
Dinophyceae				
Ceratium	Fishy	Rotten, septic medicinal	Bitter	-
Glenodinium	-	Fishy	-	Sickly sweet,oily
Peridinium	Cucumber	Fishy	-	-
Cryptophyceae				
Cryptotomonas	Violets	Violets, fishhy	Sweet	-

Source : AWWARF and LdE (1987)

Table A.3 Blue-green algae that have been identified as Geosmin and MIB producers

Blue-Green Algae	Products
Anabaena circinalis	Geosmin
Anabaena macrospora	Geosmin
Anabaena schremetievi	Geosmin
Anabaena species	Geosmin
Aphanizomenon gracile	Geosmin
Aphanizomenon species	Geosmin
Lyngbya aestuarii	Geosmin
Oscillatoria agardhii	Geosmin
Oscillatoria amoena	Geosmin
Oscillatoria brevis	Geosmin
Oscillatoria bornetii fa. tenuis	Geormin
Oscillatoria cortiana	Geosmin
Oscillatoria curviceps	MIB
Oscillatoria prolifica	Geosmin
Oscillatoria simplicissima	Geosmin
Oscillatoria species	Geosmin and MIB
Oscillatoria splendida	Geosmin
Oscillatoria tenuis	Geosmin
Oscillatoria tenuis var. levis Gardner	MIB
Oscillatoria variabilis	Geosmin
Phormidium inundatum	Geosmin
Pseudanabaena species	MIB
Schizothrix muelleri	Geosmin
Symploca muscorum	Geosmin
Synechococcus species	MIB

Sources : Persson (1983) and AWWARF and LdE (1987)

Table A.4 Odor threshold concentrations for various chemical (based upon pure substances)

Chemical	Number of Panelists (Observ.)	Threshold Odor Level ppm Average	Threshold Odor Level ppm Lowest	Threshold Odor Level ppm Highest
Acetic acid	9(9)	24.3	5.07	81.2
Acetone	12(17)	40.9	1.29	330.0
Aceptophenon	17(154)	0.17	0.0039	2.02
Acrylonitrile	16(104)	18.6	0.0031	50.4
Allyl chloride*	10(10)	14700.0	3660.0	29300.0
n-Amyl Acetate	18(139)	0.08	0.0017	0.86
Aniline	8(8)	70.1	2.0	128.0
Benzene**	13(18)	31.3	0.84	53.6
n-Butanol	32(167)	2.5	0.012	25.3
n-Butyl mercaptan	8(94)	0.006	0.001	0.06
p-Chlorophenol	16(24)	1.24	0.02	20.4
o-Cresol	13(21)	0.65	0.016	4.1
m-Cresol	29(147)	0.68	0.016	4.0
Dichloroisopropylether	8(8)	0.32	0.017	1.1
2-4 Dichlorophenol	10(94)	0.21	0.02	1.35
Dimethylamine	12(29)	23.2	0.01	42.5
Ethylacrylite	9(9)	0.0067	0.0018	0.0141
Formaldehyde	10(11)	49.9	0.8	102.0
2-Mercaptoethanol	9(9)	0.64	0.07	1.1
Mesitylene**	13(19)	0.027	0.00024	0.062
Methylamine	10(10)	3.33	0.65	5.23
Methyl ethyl pyradine	16(20)	0.05	0.0017	0.225
Methyl vinyl pyradine	8(8)	0.04	0.015	0.12
B-Naphthol**	14(20)	1.29	0.01	11.4
Octyl alcohol**	10(10)	0.13	0.0087	0.56
Phenol	12(20)	5.9	0.016	16.7
Pyradine	13(130)	0.82	0.007	7.7
Quinoline	11(17)	0.71	0.016	4.3
Styrene**	16(23)	0.73	0.02	2.6
Thiophenol	10(10)	13.5	2.05	32.8
Trimethylamine	10(10)	1.7	0.04	5.17
Xylene**	16(21)	2.21	0.26	4.13

Note : * Threshold of a saturated aqueous solution.

** Dilutions started with saturated aqueous solution at room temperature.

Source : Baker (1963)

Table A.5 Taste and odor threshold concentrations of products used in the industrial field.

Product	Threshold mg/L of water	Industry
Acetone	5 to 265 (T/O)	Paintings, varnishes, perfumery, plastics
Acetic acid	0.007 to 200 (T/O)	Printing, pothography, textiles
Allyl chloride	14700 (T/O)	Chemistry
Ammonium chloride	210 (T/T)	Chemistry
Aniline	70 (T/O)	Rubbers
Anisole	0.05 (T/O)	Chemistry
Benzene	2 to 30 (T/O)	Inks, printing, paintings, varnishes,
Bromoform	0.3 (T/O)	Chemistry
Butyl acetate	0.043 (T/O)	Perfumery, plastics, paintins
1-Butyl alcohol	0.5 to 40 (T/O)	Fungicides, insecticides, paintings, perfumery, pharmaceutics
Chloroform	0.1 (T/O)	Plastics, pharmaceutics
Cyclohexane	200 (T/O)	Oils, rubbers, photogravure
Diacetone alcohol	44.1 (T/O)	Wood, paintings, photography
1,3-Dichlorobenzene	0.02 (T/O)	Chemistry
2,4-Dichlorophenol	0.002 to 0.21 (T/O)	Chemistry
Ethyl acetate	5 (T/T)	Food, paintings, varnishes
Ethyl alcohol	100 to 2400 (T/O)	Antifreeze, explosives, perfumery, pharmaceutics
Ethyl amine	10 (T/O)	Greases, oils, resins, perfumery, pharmaceutics
Formaldehyde	50 (T/O)	Disinfectants, insecticides, textiles, coloring, plastics
Formic acid	450 to 8000 (T/O)	Galvanoplasty, textiles, metallurgy
Glucose	0.00004 (T/T)	Chemistry
Glycerol	38 to 440 (T/T)	Chemistry
Heptane	50 (T/O)	Chemistry
Heptanoic acid	3 (T/T)	Chemistry
Isobutyl acetate	0.073 (T/O)	Paintaings, solvens
Jevel water	0.05 (T/T)	Paper mills
Lactic acid	40 (T/O)	Chemistry
Magnesium sulfate	1000 (T/T)	Pharmaceutics
Methyl alcohol	10 to 1600 (T/O)	Motor fuel, paintings, varnishes
Methyl-ethyl ketone	50 (T/O)	Paintings solvents, varnishes, glue, household cleaners
Metronidazole	149 (T/T)	Chemistry

Table A.5 Taste and odor threshold concentrations of products used in the industrial field (continued)

Product	Threshold mg/L of water	Industry
Nitric acid	65 (T/T)	Chemical fertilizers, explosives, metallurgy, textiles, pharmaceutics
Nitropropane	25 (T/O)	Chemistry
1-Octanol	0.13 (T/O)	Chemistry
Oxalic acid	120 (T/T)	Household cleaners, stone polishing
Phenol	1 to 6 (T/O)	Chemistry
Pivalic acid	50 (T/O)	Chemistry
Propionic acid	20 (T/O)	Chemistry
Pyridine	0.0003 to 4 (T/O)	Chemistry
Saccharin	4.4 (T/T)	Galvanoplasty
Salicylic acid	20 to 90 (T/O)	Chemistry
Sodium chloride	450 (T/T)	Chemistry
Sodium hydroxide	320 (T/T)	Chemistry
Stearic acid	20 (T/O)	Chemistry
Styrene	0.05 to 0.73 (T/O)	Polystyrene and rubber making
Sulfuric acid	13 (T/O)	Detergents, chemical fertilizer, galvanoplasty, metallurgy
Tartaric acid	75 (T/O)	Chemistry
Tetralin	18 (T/O)	Resin solvents, greases, household cleaners, varnishes
Toluene	1 (T/O)	Painting solvents, varnishes, glue, inks, pharmaceutics, coloring, insecticides
Trichloroethylene	0.5 (T/O)	Galvanoplasty, textiles, printing, clothing
Xylenes	0.02 to 1.8 (T/O)	Paintings, printing, insecticides

Note : (T/O) = threshold odor concentration
(T/T) = threshold taste concentration
Source : Van Gemert and Nettenbreijer (1977)

APPENDIX B

Table B.1 Odor reference standards used at PWD (Philadelphia Water Department)

Compound	Concentration*	PWD Descriptive
Benzaldehyde	1000 µg/L	Almonds (sweet)
Chlorine	2 mg/L free chlorine	Chlorinous
Coumarin	1000 µg/L	Vanilla and black cherry
Cumene	100 µg/L	Shoe polish
Diphenyl ether	100 µg/L	Geranium
1-Dodecanol	2500 µg/L	Liquid dishwashing detergent (unscented)
Eucalyptol	200 µg/L	Vicks Vaporub ointment
Geosmin#	300 ng/L	Earthy (beets)
Heptanal	100 µg/L	Rancid walnut oil
2-Heptanone	500 µg/L	Sweet, banana-like organic solvent
Hexanal	200 µg/L	Lettuce heart
cis-3-Hexene-1-ol	500 µg/L	Freshly cut grass
d-Limonene	2000 µg/L	Citrus (orange, lemon, lime)
2-Methylisoborneol#	200 ng/L	Musty (peaty or brazil nuts)
Methylmethacrylate	1500 µg/L	Plastic
trans-2-Nonenal	200 µg/L	Cucumber with skin
Styrene	500 µg/L	Model-airplane glue
m-Xylene	200 µg/L	Sweet organic chemical
Cloves	Three cloves in 200 mL	Cloves (spicy)
Grass	2 g in 200 mL, several days old	Decomposing vegetation
Grass	2 g in 200 mL, one week old or older	Septic
Rubber hose	Several inches in 200 mL (boil 5 min)	Rubber hose
Soap	5 g of Ivory^R soap in 200 mL	Soapy
Wood shavings	Freshly exposed wood of sharpened pencil	Woody

Note : * The concentrations are below current toxicity levels. All compunds are diluted in odor-free water and smelled at 25°C.

The concentrations of Geosmin and 2-Methylisoborneol are much greater than their specified threshold odor concentrations.

Source : AWWARF and LdE (1987)