kluwer
the language of science

Kluwer Academic Publishers B.V.
Van Godewijckstraat 30
3311 GX Dordrecht
The Netherlands
P.O. Box 990
3300 AZ Dordrecht
The Netherlands

Manufacturing Department
T +31 (0) 78 65 76 000
F +31 (0) 78 65 76 254
I www.wkap.nl
E services@wkap.nl

Dear Author(s),

Please find attached the PDF proof of your paper which is to be published in one of our journals. Additional forms are attached for ordering extra offprints and PDF reprints (except for Book Reviews), correcting your proof, and copyright. You will not receive a paper proof nor the original manuscript.

Note: No article can be published without a signed Consent to Publish & Transfer of Copyright form in the possession of the publisher. Please sign and return this form, along with the Offprint Order form, to the address given below.

Proof Corrections

Keep your corrections to a minimum. Only essential alterations may be made at this stage. Please use the proofs solely for checking the accuracy of the typesetting as well as the completeness and correctness of the text, tables and figures. Changes to the accepted content will not be considered.

You may find it difficult to accurately judge the figure quality due to the low resolution of the PDF. If we require better quality figures you will be contacted. If your article contains colour illustrations and you would like to receive hard copy proofs of these illustrations, please contact us at the e-mail address provided below.

Finally, proofreading is your responsibility, and although the Editor may also make corrections, Kluwer Academic Publishers will not be able to proofread the paper after it has been returned, and will not assume responsibility for any errors that you have failed to correct in the proofs.

Your response, with or without corrections, should be sent within 72 hours of receipt of this material. We ask that you do not make any corrections to the electronic file (PDF); corrections and any other comments should be submitted to KAP in one of the following ways:

Corrections must be clearly marked on a printout of the PDF file and should be sent by first class mail (airmail overseas) to:

Kluwer Academic Publishers
Manufacturing Department
P.O. Box 990
3300 AZ Dordrecht
The Netherlands

or by courier:

Kluwer Academic Publishers
Manufacturing Department
Van Godewijckstraat 30
3311 GX Dordrecht
The Netherlands

Only minor corrections (±10) may be sent as an e-mail attachment to: proofscorrection@wkap.nl
Always quote the four-letter journal code and number and the PIPS No. (from your proof) in the subject field of your e-mail!

The uncorrected proof of your article will be available under “Forthcoming Papers” on the journal webpage at http://journals.kluweronline.com until publication.

Your offprints are not usually available until three weeks after publication of the journal issue, when they are sent out by surface mail. Consequently, it may take 2 to 3 months for offprints to reach authors outside Europe.

We hope you are sufficiently informed.

With kind regards,

Kluwer Academic Publishers, Manufacturing Department

kluwer
the language of science

ELECTRONIC REPRINT ORDER FORM

After publication of your journal article, electronic (PDF) reprints may be purchased by arrangement with Kluwer Academic Publishers and Aries Systems Corporation.

The PDF file you will receive will be protected with a copyright system called DocuRights®. Purchasing 50 reprints will enable you to redistribute the PDF file to up to 50 computers. You may distribute your allotted number of PDFs as you wish; for example, you may send it out via e-mail or post it to your website. You will be able to print five (5) copies of your article from each one of the PDF reprints.

Please type or print carefully. Fill out each item completely.

1. Your name: ______________________________

Your e-mail address: ______________________________

Your phone number: ______________________________

Your fax number: ______________________________

2. Journal title (vol, iss, pp): ______________________________

3. Article title: ______________________________

4. Article author(s): ______________________________

5. How many PDF reprints do you want? ____________________

6. Please refer to the pricing chart below to calculate the cost of your order.

Number of PDF reprints	Cost (in U.S. dollars)
50	$200
100	$275
150	$325
200	$350

NOTE: Prices shown apply only to orders submitted by individual article authors or editors. Commercial orders must be directed to the Publisher.

All orders must be prepaid. Payments must be made in one of the following forms:

- a check drawn on a U.S. bank
- an international money order
- Visa, MasterCard, or American Express (no other credit cards can be accepted)

Send this form with payment to:

Aries Systems Corporation
200 Sutton Street
North Andover, Massachusetts 01845
Attn.: Electronic Reprints

PAYMENT (type or print carefully):

Amount of check enclosed: __________ (payable to Aries Systems Corporation)

☐ VISA ____________________

☐ MasterCard ____________________

☐ American Express ____________________

Expiration date: __________ Signature: ____________________

Your PDF reprint file will be sent to the above e-mail address. If you have any questions about your order, or if you need technical support, please contact: support@docurights.com

TERMS OF DELIVERY

1. A minimum of 50 offprints may be ordered. Prices corresponding to the number of pages and quantities ordered are given below.

2. Author for correspondence will receive this offprint order form. This author is therefore also responsible for any orders the co-authors wish to make. All orders for a particular paper should appear together on only one form.

3. Offprints are printed at the same time the book or journal is printed. Thus, no alterations from the exact form in which the article appears in a book or journal are possible. Any orders for offprints that are received after the book or journal is printed should be submitted to the Production Secretariat at the address below.

4. Offprints will be forwarded within a short time after the appearance of the published paper.

5. No additional offprints can be printed or sent unless this order form is filled in, signed, returned with appropriate payment or official purchase order and received before the book or journal goes to press.

6. Any correspondence in connection with offprints must state the name of the periodical, title and offprint order number and name(s) of the author(s). In case of camera-ready publications please inform us as soon as possible, preferably by fax, about the number of offprints you wish to order.
All communications should be sent to Kluwer Academic Publishers, Manufacturing Department, P.O. Box 990, 3300 AZ Dordrecht / Van Godewijckstraat 30, 3311 GX Dordrecht, The Netherlands.
ABN-AMRO Bank, Dordrecht 50.80.13.917, Postal Cheque Account Number 4447384.

Prices of additional offprints are in EUR

Number of copies	Number of pages					
	1-4	5-8	9-12	13-16	17-20	+4
50	108	177	248	318	388	71
100	153	238	323	407	492	85
150	200	300	400	500	599	100
200	246	361	476	591	706	115
250	292	422	551	681	810	130
300	339	483	628	772	917	145
350	385	544	703	863	1022	159
400	431	606	780	955	1129	175
450	478	667	857	1046	1235	189
500	524	728	932	1136	1340	204
+50	+50	+62	+72	+92	+103	+15

Payment will be accepted in any convertible currency. Please check the rate of exchange with your bank.
If ordering from within The Netherlands please add 6% VAT to the price quoted above.

As of January 1st 1993 customers within the EEC must consider the following rules:

- **If you are in possession of a VAT identification number, please fill the VAT number in on the order form. You will not be charged VAT.**
- **If you do *not* have a VAT number, then please add the low VAT rate - applicable to your country - to the prices quoted above.**

kluwer
the language of science

PROOF CORRECTION MARKS TO BE USED BY AUTHORS

MARGINAL MARK	MEANING	CORRESPONDING MARK IN TEXT	
δ	Delete (take out)	/ or ⊢⊣	Cross through
δ̑	Delete and close-up	⁀/⁀ / ⊖	Above and below matter to be taken out
stet	Leave as printed (when matter has been crossed out by mistake)	-----	Under matter to remain
caps.	Change to capital letters	≡	Under letters or words altered
l.c.	Change to lower case letters		Encircle letters altered
bold	Change to bold type	∼∼	Under matter altered
bold ital.	Change to bold italic type	≈	Under matter altered
ital.	Change to italics	—	Under matter altered
rom.	Change to roman type		Encircle matter altered
×	Replace by similar but undamaged character or remove extraneous marks		Encircle letter to be altered
γ	Insert (or substitute) superior figure or sign	ʎ or /	
λ	Insert (or substitute) inferior figure or sign	ʎ or /	
⁀-‿	Insert (or substitute) hyphen	ʎ or /	
EN |—|	Insert (or substitute) dash	ʎ or /	
(/)	Insert (or substitute) solidus	ʎ or /	
...	Insert (or substitute) ellipsis	ʎ or /	
⁀‿	Close-up–delete space	⁀‿	Linking words or letters

#	Insert space	I or Ƴ	Between items
equal #	Make spacing equal	I	Between items
⊤	Reduce space	I or ⊤	Between items
≻—	Insert space between lines or paragraphs		
←	Reduce space between lines or paragraphs		
⊔⊓	Transpose	⊔⊓	Between letters or words, numbered when necessary
⊆	Transpose lines	⊆	
centre	Place in centre of line	] [	Around matter to be centred
⊢[ ]	move to the left	]	
[ ]⊣	move to the right	[	
NP	Begin a new paragraph	□	Before first word of new paragraph
run on	No fresh paragraph here	⟵⟶	Between paragraphs
ʎ	(Caret mark.) Insert matter indicated in margin	ʎ	
‘γ ’γ “γ ”γ	Insert single/double quotes	ʎ ʎ	

Remarks

To indicate a substitution, simply cross out the letters or words to be replaced, and write the correct letters or words in the margin. It is not necessary, nor even desirable, to use the marks for *delete* and *insert* when making a substitution. If there is more than one substitution in a line, place them in the correct order in the margin, and indicate the end of each correction with an oblique stroke / . Alternatively, continental location marks may be used, but these are to be placed in front of the corrections, not behind as in the case of the oblique stroke.

The typesetter treats *all* letters and words in the margin as insertions or substitutions, so – to avoid misunderstanding – any comments *not* intended to form part of the text should be encircled.

All alterations should be marked clearly so that there is no risk of misunderstanding; long additions or amendments should be typed on separate slips and attached. *Only really essential alterations should be made at proof stage.*

In addition to reading the proofs, please look through your edited manuscript to see if there are *any queries from the copy editor*, and if so, answer the queries *on the proofs.*

Re/Views in Environmental Science & Bio/Technology **00:** 1–11, 2004.
© 2004 *Kluwer Academic Publishers. Printed in the Netherlands.*

Review

Olfactory and chemical analysis of taste and odor episodes in drinking water supplies

I.H. (Mel) Suffet[1], Linda Schweitzer[2] & Djanette Khiari[3]
[1]*Environmental Health Sciences, Environmental Science and Engineering Program, UCLA School of Public Health, LA, CA 90095, USA;* [2]*Department of Chemistry, Oakland University, Rochester, MI 48309, USA;* [3]*American Water Works Association Research Foundation, Denver, CO 80625, USA*

Key words: drinking water standards, flavor profile analysis, odor descriptors, taste and odor wheel

Abstract

This paper evaluated the present knowledge of taste and problems in drinking water supplies in the form of a “Taste and Odor Wheel” which organises the relationships between specific taste and odor problems and their causes. The Flavor Profile Analysis (FPA) method enabled the development of the odor descriptors on the wheel. The abilities and short-comings of the FPA method for odor evaluation by taste and odor panels were evaluated. The present state of development of taste and odor standards for drinking water was then discussed.

Introduction

All over the world, consumers judge the quality of the water they drink mainly by its aesthetic properties of taste and odor. Consumers expect their drinking water to taste good, and often associate the presence of off-flavors in the water with potential health risks. This perception of water quality is often translated into a lack of trust of the treated water industry and has resulted in a dramatic increase in the use of bottled water in the last two decades. This mindset has led the water industry and the scientific community to dedicate significant financial resources and research efforts to understanding and solving taste-and-odor problems in drinking water.

Various organisms and chemicals causing taste-and-odor problems in source water and in distribution systems have been identified (Mallevialle & Suffet 1987; Suffet et al. 1995). This progress has been made possible by the combined use of highly sophisticated analytical techniques such gas chromatography/mass spectrometry and sensory-gas chromatography and sensory panel analytical techniques, especially the Flavor Profile Analysis (FPA) introduced by Metropolitan Water District (MWD) of Southern California in the 1980’s (Krasner et al. 1985). FPA was traditionally used in the food and beverage industry and was modified and adapted for use in the drinking water field. FPA determines the specific characteristics of a water sample and the intensity of each individual characteristic, without dilution.

This paper will evaluate the frame of reference of our present knowledge of taste and problems in drinking water supplies in the form of a “Taste and Odor Wheel”. The “Taste and Odor Wheel” organizes the relationships between specific taste and problems and their causes. The development of the Taste and Odor Wheel was made possible by the use of FPA panels assigning odor descriptors and the intensity of each odor descriptor by the FPA method, instead of the dilution to threshold approach of the threshold odor number (TON). Thus, the abilities and shortcomings of the FPA method for odor evaluation by taste and odor panels will be evaluated. Then, the “Year 2000 Taste and Odor Wheel” is described (Suffet et al. 1999). Finally, the paper will discuss how our present state of knowledge of taste and odor problems can be used to develop so-called Secondary US Drinking Water Standards for tastes and odors for Drinking Water Supplies.

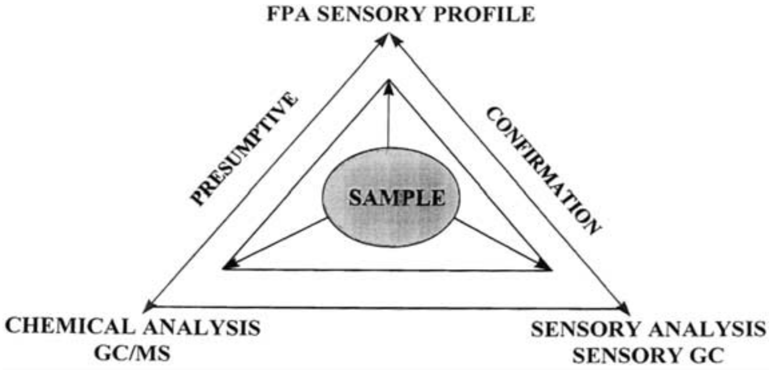

Figure 1. Schematic diagram of relationship between instrument and sensory methods.

Evaluation of taste and odor problems in drinking water

The literature is filled with presumptive statements about the causes of taste and odor problems, which can be misleading to the water industry. Rules of evidence describing "the scientific method" are used to define presumptive and confirmatory testing procedures to validate the cause of a taste and odor event in drinking water (Mallevialle & Suffet 1987; Persson 1992). In short, Figure 1 shows the odor triangle that can be used to develop a presumptive statement and a confirmatory statement about the causes of taste and odor problems. First, Figure 1 shows that in determining the chemical causes of taste and odor problems requires developing a presumptive statistical correlation between the chemical compounds in the water sample and the tastes or odors by sensory panel techniques and separating and identifying those individual compounds that have the same sensory characteristics as the whole water sample, as described by a sensory panel, by sensory GC analysis (Khiari et al. 1992). Figure 1 shows that final confirmation is completed by having the sensory panels evaluate the chemical identified by FPA.

Sensory panel analysis

Sensory methods are used to assess the qualitative description of a taste or odor and rate it on an intensity scale. Sensory methods often are more sensitive than analytical instrumentation-based methods. The reason many chemicals are of taste-and-odor concern is due to their low odor thresholds. The odor thresholds of these compounds are often below instrumental detection limits.

Standard Methods for the Examination of Water and Wastewater (APHA et al. 2000) includes three methods for evaluating taste and odor: The flavor threshold test (FTT), also called threshold odor number, the flavor rating scale (FRS), and flavor profile analysis. TON consists of performing successive dilutions of the water sample with reference water and comparing each dilution with the reference water. The highest dilution in which odor is perceptible is the TON. A TON less than or equal to 3 passes the US and European secondary drinking water standards. The limitations with TON are that no descriptive information about the odor is provided, so this test cannot be used to determine the source or cause of a taste-and-odor event, and upon dilution, the type of odor that is smelled can change and thus the effect of each odor type is not defined.

FPA, unlike TON and FRS, requires no dilution and fewer samples, and is therefore suitable for monitoring source water and the entire treatment process, from raw to finished waters. Since FPA directs panelists to record descriptors for all tastes-and-odors, it the most valuable method for forensic purposes. For each FPA descriptor, a quantitative 7 point scale is used; threshold [ )(or 1]; slight [2]; weak [4]; medium [6]; medium strong [8]; strong [10]; very strong [12]. It has been observed that consumers can easily identify an off-flavor in drinking water when a descriptor with an intensity level of above 4, occurs e,g, musty, 4. It is pointed out that individual consumers have different threshold concentration levels and some people are anosmic (i.e., cannot smell) a specific odor. FPA requires only a few panelists to test undiluted samples, however, the panelists have to be highly trained. Once panelists are trained, FPA is a relatively inexpensive method of analysis, and is very quick compared to other methods. The major criticism of FPA besides the requirement for trained panelists, is that it is not a statistical method, and is therefore more subjective. Also, certain personality traits (e.g., dominant types) can influence other panelists, and the skill of the FPA leader is essential for leading the panel to consensus.

New approaches presently combine statistical methods with FPA. Profile Attribute Analysis (PAA), used in the food and beverage industry, is a statistical method that employs aspects of FPA (Neilson et al. 1988; Meilgaard 1999). PAA still requires consensus, and is based closely on FPA, but with the introduction of numerical scales. Average scores are used instead of arriving at a consensus number and data are analyzed using parametric techniques such as ANOVA. A statistical approach can reduce biases and, in general, give more accurate results. Meilgaard (1999) provides the details for designing and evaluating statistical methods for sensory analysis.

The relationship between the chemical concentration in actual water samples and the odor intensity is determined by the sensory panels using the FPA method (APHA et al. 2000). The descriptive component is presented below in terms of the Taste and Odor Wheel. The relationship between odor intensity and odorant concentration in water can be described by either of the two following models:

(1) Weber-Fechner model (Thiemer 1982): Intensity = m log (concentration) + b,

where m is the slope and b is the y intercept, or

(2) Stevens' Power model (Moskowitz et al. 1974): Intensity = k (concentration)^n where k is a proportionality constant and n is a exponential constant.

An exponent (n) of less than 1.0 indicates that a change in intensity results from a greater change in odorant concentration (the sensory ratio is smaller than the physical ratio), which is generally true for odors that follow the Weber-Fechner model. For the Stevens' Power model, an exponent of 0.5 would mean that an increase of 1 to 10 in concentration corresponds to an increase of 1 to 3.2 in odor intensity. Three reference standards were evaluated to obtain a dose-response relationship: geosmin, 2-MIB, and n-hexanal (Burlingame et al. 1991a). The expected concentrations agreed fairly well at low odor intensities for both the Weber-Fechner and Stevens' Power Law models, but the Stevens' Power Law model produced less deviation at higher odor intensities. For multi-component odors in drinking water, antagonism between odors can occur, e.g., chlorine can mask the earthy and musty odors of geosmin and 2-MIB, respectfully (Worsley et al. 2003).

A crucial element in the prevention and control of taste and odor problems consists of a regular monitoring program of source and finished water. FPA can be used for the early detection of taste and odor compounds by monitoring taste-and-odors in water and for determining quantitatively what levels of a specific odorant evoke consumer complaints. Simplified versions of FPA also can be used. Three new alternative sensory methods include the Specific Attribute Rating Test, the 2-of-5 Odor Test, and a rating method for evaluating distribution system odors in comparison to a control (Dietrich et al. 2001).

The newer alternative methods require simpler training and less time to perform. Eight water utilities from North America and Asia are currently using these new methods. The new tests include:

- The *Attribute Rating Test* evaluates the presence or absence of a chemical. The method allows for the rating of the intensity of an odorant, such as geosmin or 2-methyl isoborneol (MIB). A standard is provided at a concentration at which consumer start to complaint. Using a "paired-comparison" format, water samples are compared to the intensity of the standard and rated as either not detected, less than, equal to, or greater than the standard.
- The *2-out-of-5 Odor Test* is designed to determine noticeable differences between water samples. The test applies to routine monitoring of raw or finished water to detect odor changes over time and tracking odor problems in watersheds by comparing water samples taken from different locations in the watershed. The 2-out-of-5 Test is a forced comparison test, requiring only 1 to 5 persons with minimal training. The panelist(s) have to sort 5 samples into two groups – one group of two flasks that are identical, and one group of 3 other flasks that are identical, but different from the group of 2. If the panelist(s) correctly identify the two samples that are similar, but different to the other three samples, there is only a 10% chance that they could have guessed the right answer. Therefore, this method is statistically sound. This approach could be used to determine if a source of water really has an odor that consumers may notice. A reference standard could be compared to a source of water in question to determine if it is likely that consumers will notice the odor compared to what they are used to drinking.

- *Rating Method for Evaluating Distribution System Odors in Comparison to a Control.* This test compares the difference between a control water and distribution system water in order to identify odorous substances that are not usually present in finished water leaving the plant. It requires one test administrator and two panelists. All samples are compared to a control which is a water sample that is deemed representative of the utility's ideal or typical water before it goes through the distribution system, or it could be an odor-free water. The distribution system water samples are compared to the control and rated as much weaker, slightly weaker, same, slightly stronger, or much stronger than the control. Descriptors are recorded. This is much like FPA, except instead of using intensities, the ratings are used, so it is easier,

The Taste and Odor Wheel

A better understanding of the chemical causes of tastes and odors in drinking water helps control of taste and odor problems. The descriptive component of the FPA test has enabled major advances in the study of tastes and odors in water in the last twenty year. These studies have been summarized in the Taste and Odor Wheel for the drinking water industry that is continually upgraded (Mallevialle & Suffet, 1987; Brady et al. 1988; Suffet et al. 1988, 1995, 1999; Burlingame et al. 1991a). Figure 2 shows the Taste and Odor Wheel which includes eight classes of odors, four tastes, and a mouth feel/nose feel category. Two different philosophies were used as a guide in developing the Taste and Odor Wheel. First, the Taste and Odor Wheel is to be used to help develop a common language for taste and odor sensory panels and drinking water practitioners. Second, the Taste and Odor Wheel is devised to present to the water industry the current knowledge about the identification of the "common" organoleptic characteristics found in drinking water. The Taste and Odor Wheel describes primary taste and odor categories (inner circle), those common tastes and odors from each primary category that are defined by trained sensory panels (outer circle). The chemicals that have been confirmed as the cause of taste and odor problems in drinking water are noted by a $*$ (outside the circles). All the other chemicals that are listed outside the two circles, without a star, have been used by sensory panels as "Representative" of the odor defined for the particular organoleptic response (Burlingame et al. 1991a).

The Taste and Odor Wheel presents some reference standards for odors. However, odor descriptors are often related to individual experiences. Also, odors in the earthy/musty category can be produced by several different compounds, such as geosmin, 2-MIB, and 2,4,6-trichloroanisole (TCA). Often, differentiation can be accomplished only by direct comparison between the odor and the chemical. For example, a novice panel may describe both geosmin and 2-MIB as earthy/musty using the inner circle of the wheel, whereas a highly trained panel may describe a standard of geosmin in distilled water by its refined descriptors in the second band of the wheel such as earthy, wet mud, beet, river-bed odor.

A third category of reference standards besides the "Known" and "Representative" (Burlingame et al. 1991a) compounds on the outside of the odor wheel is also important for FPA standards: the so-called "Substitutes" are standards that are made from natural materials producing an odor that occurs in water and can be prepared in a consistent manner. Examples include decayed vegetation and septic odors made from aged solutions of grass (APHA et al. 2000). The ultimate goal is to develop an odor reference standard library and to move representative odorants to identified compounds. For example, the representative compound for the grassy odor was determined to be *cis*-3-hexen-1-ol, which is one of the actual causes of the grassy odor in water (Khiari et al. 1995a). Known references, such as *cis*-3-hexen-1-ol that occur in raw and treated drinking water then are evaluated for their odor threshold concentration (OTC) and for dose-response relationships (Khiari et al. 1995a). An understanding of these relationships can help explain the impact of odorous compounds on the overall sensory quality of drinking water.

However, there is still a general lack of identification of compounds that cause taste and odor problems, especially when compounds are present in complex mixtures at or below an individual OTC. A combination of odorants can interfere with the identification of individual odorants. Some chemicals can mask other odors (serving as antagonists), or act synergistically to make the odors seem stronger than what the intensities would be if present individually. Also, a chemical's odor characteristics may change as a function of concentration, or may change for other reasons. For example, as algae grow, they can produce odors that progress from cucumber to fishy as their abundance or growth cycle changes (Rashash et al. 1993). Also, odor-causing compounds may volatilize, hydro-

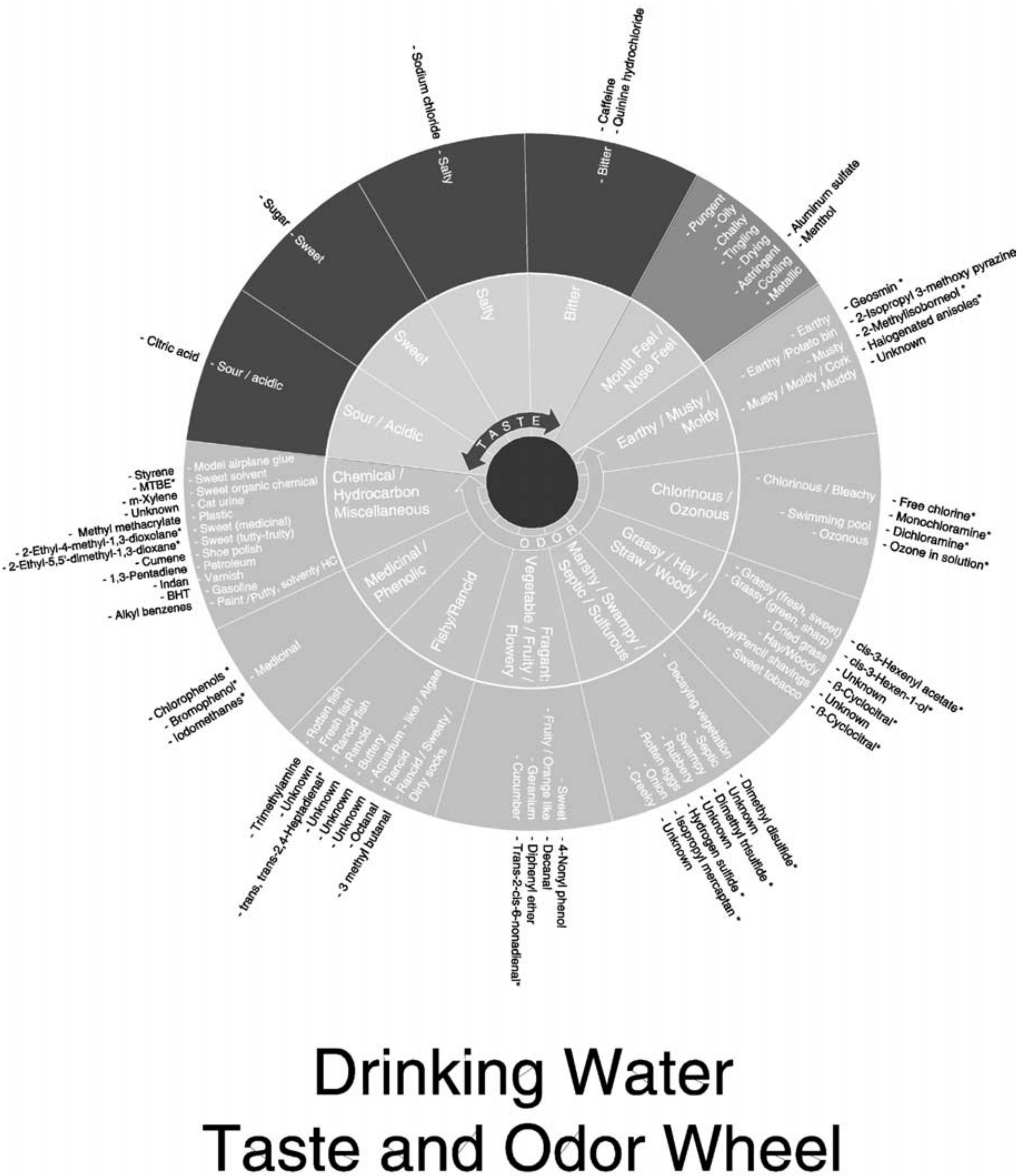

Figure 2. Taste and Odor Wheel “2000” (Suffet et al. 1999).

lyze, photolyze, or biodegrade during a taste and odor episode or during the sampling and analysis steps (Khiari et al. 1999a).

The above examples illustrate the difficulties in identifying sources and causes of taste-and-odors. The Taste and Odor Wheel (Suffet et al. 1999) is really a starting point in a forensic investigation. The categories and examples of how they can be used to determine the sources of taste and odor events are summarized below.

Earthy/musty/moldy

Geosmin, 2-MIB, and TCA have been identified in water supplies as odorants of this group, with OTCs of $<$ 10 ng/L (Mallevialle & Suffet 1987). Geosmin and 2-MIB have been isolated metabolites of many genera of algae in drinking water supplies. Recently, TCA has been confirmed to be produced in water distribution systems (Montiel 1991; Nystrom et al. 1992) and has an OTC of about 20–80 pg/L (UKWIR 1996). In water distribution systems, trichlorophenols, which are chlorination by-products, can be transformed to trichloranisoles via the methylation process (Montiel et al. 1991). Montiel et al. (1991) showed that a phenol concentration of 0.1 μg/L was sufficient to produce a musty taste. Other chemicals than geosmin, 2-MIB, and TCA may produce earthy/ musty odors, as these types of descriptors are reported by FPA panels when these chemicals are not identified by chemical analysis (Bruchet 1999).

Chlorinous and ozonous

Hypochlorous acid and hypochlorite ions have the same odor descriptor, "bleach". Hypochlorous acid has a pK_a of 7.6 and ionizes to hypochlorite ion and hydronium ion. Hypochlorous acid ($pH < 6$) has an OTC of 0.28 mg/L, whereas hypochlorite ion ($pH > 9$) has an OTC of 0.36 mg/L (Krasner & Barrett 1984). The breakpoint chlorination curve describes the reaction of chlorine and ammonia. The dominant chlorine species in water prior to the breakpoint are monochloramine and dichloramine, with an odor descriptor of "swimming pool". According to data from the Metropolitan Water District of Southern California, mono-chloramine at concentrations of 0.5 to 1.5 mg/L has an intensity level to 2.0 (very slight) on the seven-point FPA scale Monochloramine rarely causes taste and odor problems in drinking water unless its concentration exceeds 5 mg/L (Krasner et al. 1986) The OTC of monochloramine is 0.65 mg/L (Krasner & Barrett 1984). Dichloramine in concentrations of 0.1 to 0.5 mg/L in water has an odor intensity level of 4 (slight) to 8 (moderate). However, if the concentration of dichloramine reaches 0.9 to 1.3 mg/L, the odor will be described as moderate to very strong, which is offensive and not acceptable. Most people perceive the unpleasant chlorinous smell once the concentration of dichloramine is above 0.5 mg/L (Krasner & Barrett 1984).

Fragrant: Vegetable/fruity/flowery

The cucumber odor in drinking water has been determined to be *trans,cis*-2,6-nonadienal (Burlingame et al. 1991b). Although a general vegetable odor and specific vegetable odors have been observed by FPA panels, more studies are needed to identify the specific compounds associated with these odors.

High-molecular-weight aldehydes greater than C-7 (heptanal), showed a positive statistical correlation with fruity odors produced during the ozonation drinking water process, a presumptive test of a chemical cause of an odor (Anselme et al. 1988). In an independent sensory panel study, a Weber-Fechner relationship was developed between a fruity odor intensity measured by an FPA sensory panel and the logarithm of the total aldehyde concentration in a mixture of seven straight-chain aldehydes (C-6 to C-12). This is a sensory confirmation of a chemical cause of an odor. The fruity/orange-like odor of decanal is used to represent this group of aldehydes.

Medicinal

The chloro- and bromophenols are in the medicinal class (e.g., iodoform, phenolic, medicinal). The OTC order follows approximately the same pattern as the chlorophenols, i.e., 2-bromophenol and 2,6-bromophenol have the lowest OTC, with 30 ng/L and 0.5 ng/L, respectively, as reviewed by Suffet et al. (1995b). The formation of bromophenols is also a function of pH and follows the same pattern as chlorophenols. The formation of brominated and iodinated haloforms in drinking water can occur by chlorination of bromide or iodide with free chlorine and the subsequent reaction with natural humic material. As a result, the presence of iodinated haloforms at concentrations between 0.30 and 10 μg/L will cause medicinal taste and odor problems in drinking water (Gittelman & Yohe 1989; Bruchet et al. 1989).

Grassy/hay/straw/woody

Two grassy compounds have been confirmed in drinking water supplies (*cis*-3-hexen-1-ol and *cis*-3-

hexenyl acetate) (Khiari et al. 1999a). When grass was allowed to decay in water, the first compound to be released in the water was the acetate which can biologically or chemically hydrolyze at pHs >6.1 to the corresponding alcohol (Khiari et al. 1999). *cis*-3-hexenyl acetate exhibited a low OTC of 1–2 μg/L, only 2–4 percent of the OTC of *cis*-3-hexen-1-ol (Khiari et al. 1995a).

The compound, β-cyclocitral, has been identified in lake and treated water during an algae bloom to cause hay/woody odors (Young et al. 1999). This work demonstrates the importance of knowing the relationship of odor type and concentration, as provided by the Weber-Fechner Curve, as β-cyclocitral changes odor with concentration. Only between 2 and 20 μg/L does it have a hay/woody odor in distilled water. β-Cyclocitral has been described as having a tobacco type of odor (Slater & Block 1983) at higher concentrations.

Fishy/rancid

Trans,*trans*-2,4-Heptadienal, a metabolite of the algae *Uroglena americana*, is described as contributing to the fishy odor in the Nunobiki reservoir in Japan (Yano et al. 1988) and in a California reservoir (Khiari et al. 1995b). The Weber-Fechner Curve for *trans,trans*-2,4-heptadienal gives an OTC of about 5 μg/L with a rancid fishy odor (Young & Suffet 1999). There is a pH dependence on the stability of the *trans,trans*-2,4-heptadienal (Suffet 1999). This compound is more stable near pH 9, and samples should be collected and preserved at high pH and refrigerated when collected for analysis. This contrasts with the stability of grassy compounds at low pH (Khiari et al. 1999). Sensory GC analysis has indicated that *trans*-4-heptenal is associated with fishy odors, and 1-pentene-3-one is associated with rancid odors (Khiari et al. 1995a); however, these identifications need further confirmation. The odor at the olfactory port of the GC indicated at low concentrations in one case as a rancid odor and in another case as a fishy odor.

Rancid, buttery, and soapy odors have been also observed from ozonation of drinking water (Crozes et al. 1999) and are added as unknowns to the "Taste and Odor Wheel". These odors have also been observed during sensory GC analysis (Khiari et al. 1995b). The identification of specific rancid, buttery, and soapy odors needs further study.

Marshy/swampy/septic/sulfurous

Dimethyl disulfide has been identified as one component of the decaying vegetation odor by Sensory GC (Khiari et al. 1997). Generally, when dimethyl disulfide is present, other compounds have been identified by GC sensory analysis with decaying vegetation odors. These include 2-isobutyl-3-methoxpyrazine, identified as a vegetable odor, and 2-isopropyl-3-methoxypyrazine, identified as a rotten vegetable odor (Khiari et al. 1997). However, the literature indicates that the odors associated with the pure 2-isobutyl-3-methoxypyrazine compound are earthy/musty and bell pepper, and for the pure 2-isopropyl-3-methoxypyrazine compound, they are earthy-musty and potato bin. The effect of concentration of the combination of these chemicals appears to need further investigation in the presence of dimethyl disulfide.

Dimethyl trisulfide may be associated only with the swampy odor (Khiari et al. 1997). Both dimethyl trisulfide and indole have been found to have odor characteristics similar to the odors found in samples analyzed by FPA, but they were not sufficiently extracted from the water to produce odors at the olfactory port of the sensory GC. Thus, at present, it is suspected that dimethyl trisulfide and indole may contribute to the septic odor (Khiari et al. 1997).

Chemical/hydrocarbon/miscellaneous

Of the many compounds in this group, the most recent odor episodes in drinking water have been with by-products of resin manufacturing and oxygenated fuels used for smog reduction. Resin manufacturing has produced sweet (tutti-frutti) – 2-ethyl-5,5'-dimethyl-1,3-dioxane (2-EDD) from the reaction of propionaldehyde and neopentyl glycol – and sweet (medicinal) – 2-ethyl-4-methyl-1,3-dioxolane (2-EMD) from the reaction of propionaldehyde and propylene glycol. 2-EDD and 2-EMD have OTCs of < 10 ng/L. These compounds have been identified in the Neshaminy Creek, Pennsylvania (Pretti et al. 1993), in groundwater in an aquifer near Barcelona, Spain (Ventura 1995) and in the Ohio River (Noblet et al. 1999),

Methyl *tertiary*-butyl ether (MTBE) used in oxygenated fuel for smog reduction is a compound of particular concern in leaky underground storage tanks that has been found to affect groundwater supplies and in drinking water reservoirs and lakes from fuel usage from two-cycle outboard motors. The OTC of the MTBE odor is described as a sweet/hydrocarbon odor, with an OTC at 15 μg/L (Stocking et al. 1999).

Table 1. Development of Secondary Drinking Water Standards

	Standard	Comments	Reference
Organization			
US EPA, Secondary Drinking Water Standard	TON = 3 @60 °C	Does not describe: 1. odor strength 2. mixtures of odorants 3. correlation with customer complaints 4. objectionable odors every time 5. changes from dilution	USEPA 1979; EC 1975; USFDA 1979
Phase II, 1989 Amendment to Safe Drinking Water Act	OTC of 7 chemicals	1. No Data available on OTC in Water 2. TON retained at 3	USEPA 1991
US EPA – MCLs	Chemicals	Some chemicals OTC are < MCLs	USEPA 1998
California, US – enforceable Secondary MCL	MTBE = 5 ug/l		California Registry 1999
Suggestions			
Individual utility – treatment goal	Chemical	1. Question of variable sensory response 2. Effect of matrix	AWWA, T&O Committee Report 2002
AWWA T&O Committee for all utilities	OTC for chemicals	1. Question of variable sensory response 2. Effect of matrix	AWWA, T&O Committee Report 2002
AWWA T&O Committee for all utilities	Frequency of presence; 10%/month?	1. Question of variable sensory response 2. Effect of background matrix 3. Panel type and preparation	AWWA, T&O Committee Report 2002
AWWA T&O Committee for all utilities	Treatment option	1. Question of variable sensory response 2. Effect of matrix	AWWA, T&O Committee Report 2002
AWWA T&O Committee for all utilities	Surrogate standard	1. No correlations are available. (algae counts, algae types or any parameter)	AWWA, T&O Committee Report 2002
AWWA T&O Committee for all utilities	OTC for chemicals	1. Question of variable sensory response 2. Effect of matrix	AWWA, T&O Committee Report 2002
Individual utilities-community based	OTC for chemical adjusted to % of acceptance	1. Eliminates variable sensory response 2. Includes matrix	This paper
USA based	FPA intensity	1. Develop with utilities.	This Paper

Secondary US EPA Drinking Water Standards

Our present state of knowledge of taste and odor problems can be used to develop so-called Secondary US EPA Drinking Water Standards for taste and odor for Drinking Water Supplies. A secondary standard is not enforceable as a primary US EPA Drinking Water Standards. It really is a “target value” or “control-limit” and can be described as such by a water utility to its consumers. This development of secondary standards has begun in earnest with the saga of methyl tertiary butyl ether (MTBE) groundwater pollution, as an enforceable drinking water standard in the state of California in the US. MTBE is a gasoline additive that is now being phased out of use because it was contributing to taste-and-odor problems in groundwater and was determined to be of health concern; however, to date its toxicity is not fully understood.

The regulatory attempts to make secondary drinking water standards are outlined on Table 1. The

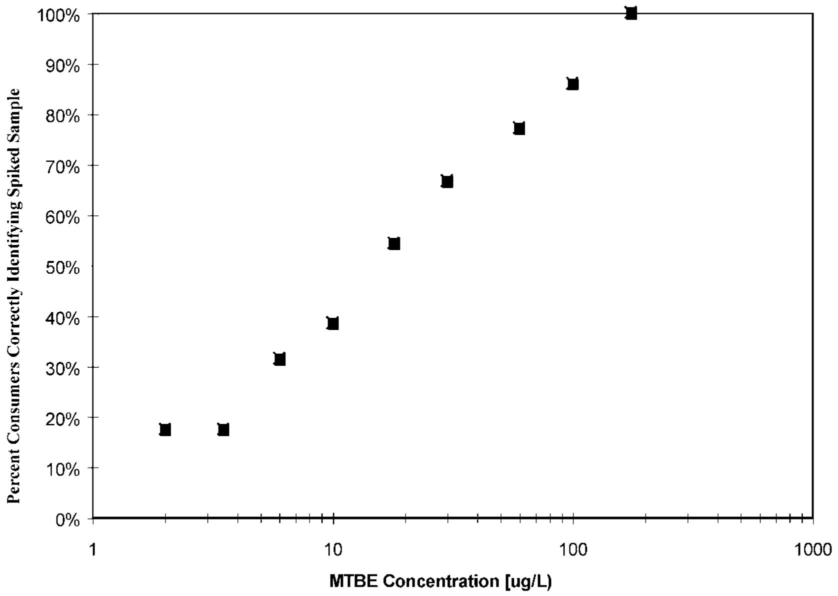

Figure 3. Distribution of odor threshold concentrations for MTBE.

problems with each of the approaches are defined in the Table. At present, the last two approaches are suggested. The first suggestion of an individual utilities-community based standard is based upon OTC for a chemical adjusted to % of community acceptance is presented as a viable option. Figure 3 shows how this would work to develop a standard for MTBE Stocking et al. 1999).

A study must be completed by a consumer panel for the OTC by the ASTM "forced choice" Method ASTM E-679-91, (Stocking et al. 1999) in the water at that locality. Figure 3 defines the % of acceptance vs the odor concentration. The OTC was calculated to be 15 ug/L, and represents the threshold of the median of the 57 consumers (assuming a log-normal distribution) in distilled water. If the community decides to pick a % acceptance of $<$ 20%, then the acceptable secondary standard is 3.5 ug/l. The application of these results to establish a Secondary MCL for MTBE has no prior precedent. In practice, consumers would be exposed to MTBE in a natural water matrix that may be synergistic or antagonistic to the odor of MTBE. Experience from LaCrosse, Kansas, where consumers were repeatedly exposed to MTBE concentrations greater than 100 ug/L without voicing complaints, revealed that a natural water matrix with high hardness or TDS could mask the odor of MTBE (California MTBE Research Partnership 2000; Maine DHS 1998). Therefore, optimally, the OTC at a water utility should be determined in the water matrix of the utility. Alternatively, a water utility could just use Figure 3 as a model for a standard, but this is not judged to be the optimum approach.

The criterion A of the Safe Drinking Water Act Secondary MCL guidance is intended to prevent a *substantial number of persons ... to discontinue [public water system] use (US EPA 1991).* There is no indication of whether the term *substantial* should represent 50% of the population, 75% of the population, or even 95% of the population. Since the TON of 3 is deemed acceptable, the present SMCL is *not* meant to protect the most sensitive individuals from objectionable tastes or odors in drinking water and this implies that there is an acceptable odor for drinking water.

A second approach in Table 3 for a utility based standard is the guidance of an FPA intensity of, for example, 3 of a descriptor; e.g., musty 3. The utility FPA panel can be correlated with consumer recognition to set a level which triggers taste and odor treatment, e.g., PAC usage. If a weekly program of evaluation is augmented by the awareness and training of treatment personnel, this can be instituted. This is the approach in general taken at the Philadelphia Suburban Water Co., Bryn Maw, PA and the Metropolitan Water District of Southern California, Los Angeles, CA.

Discussion

The “Taste and Odor Wheel” developed over the last 20 years includes compounds identified in the eight classes of odorants, four tastes, and one mouth feel/nose feel category. Over the last ten years, many types of odors have been identified by sophisticated instrumental analyses – e.g., gas chromatography/mass spectrometry (GC/MS), and sensory methods such as Flavor-profile analysis (FPA). A combination of approaches is still needed to determine sources of contaminants that cause taste-and-odor problems in drinking water. It is important to determine the source, including the specific chemical(s) that cause certain tastes-and-odors in order to provide water utilities with the information they need to prevent a taste-and-odor event from occurring, or provide solutions such as treatment options to mitigate the problem. Once a new contaminant is identified, this could also lead to the development of a new water quality standard.

Despite this progress, there are areas that require further investigation:

- There are numerous types of tastes and odors that may correspond to a group of chemicals and not to one chemical. In other words, one odor descriptor may correspond to many different chemicals and this must be evaluated.
- Sensory descriptors that change with concentration of the chemical present must be understood.
- Very little is known of the behaviour of taste and odor compounds in mixture. What are their synergism/antagonism effects between taste and odor compounds?
- Taste and odor compounds can originate from numerous locations including source contamination, microbial metabolites, chemicals produced during treatment and chemicals produced in the distribution system. These must be defined to minimize problems.
- The localized and transient nature of taste-and-odor problems makes them difficult to study. Methods to quickly define sources of the problem must be to understand the cause of the problem.
- There are few, if any, enforceable regulation of taste-and odor compounds in drinking water worldwide. Taste and odor regulations have the status of secondary standards. For example, secondary Maximum Contaminant Levels for odor are listed as “3” on the threshold odor scale in the US. Yet, control of taste and odor events are not correlated with this scale. New approaches are suggested: ASTM force choice analyses and OTC adjusted to 100% of acceptance.

For the science of taste and odor to continue to advance, more effort needs to be spent to characterize the taste and odor types and to develop analytical procedures to identify causes of the problems so that economical solutions can developed to forewarn and/or minimise taste and odor events. In the future, will an electronic nose or a genetically coded nose receptor be able to detect off-odors, perhaps as an early warning sensory system-?

References

American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation (2000) Standard Methods for the Examination of Water and Wastewater, 20th ed. APHA, Washington, D.C., USA

American Water Works Association, Water Quality Division, Taste and Odor Committee (2002) Committee Report: Options for a taste and odor standard. Jour. AWWA 94: 80–86

Anselme C, Suffet IH & Mallevialle J (1988) Effects of ozonation on tastes and odors. Jour. AWWA 80: 45

Brady B, Bartels JHM, Mallevialle J & Suffet IH (1988) Sensory analysis of drinking water. Wat. Qual. Bull. 13(2/3): 61

Bruchet A, N’Guyen K, Mallevialle J & Anselme C (1989) Identification and behaviour of iodinated haloform medicinal odor. Proceedings AWWA Ann. Conf., Los Angeles, CA, USA

Burlingame GA, Khiari D & Suffet IH (1991a) Odor reference standards: the universal language. Proceedings AWWA Wat. Qual. Technol. Conf., Orlando, Fla., USA (pp. 7–39)

Burlingame GA, Muldowney JJ, Taylor I & Maddrey RE (1991b). Cucumber flavor in Philadelphia drinking water. Jour. AWWA 83: 92

California MTBE Research Partnership (2000) Treatment tecnologies for removal of metyl teriary butyl ether (MTBE) from drinking water, 2nd ed. Center for Groundwater Restoration and Protection. National Water Research Institute, Irvine CA, USA, Feb. 2000. NWRI-99-06

California Registry (1999) Final statement of reason for secondary maximum contaminant level for MTBE and revisions to the unregulated chemical monitoring list R 44–97, Title 22 California USA, Code of Regulations, 64449

Crozes G, Hangstrom J, Suffet IH & Young C (1999) Bench-scale evaluation of adsorptive processes for taste and odor control using rapid small scale column tests and flavor profile analysis. Wat. Sci. Technol. Wat. Sci. Technol. 40(6): 39–44

Dietrich AM, Hoehn RC, Hiltebrand D, Johnson M, Khiari D, Waer M, Whelton AJ & Worley J (2001) New practical methods for sensory analysis in drinking water: beyond threshold odor number (TON) and Flavor Profile Analysis (FPA). Workshop S5, Water Quality Technology Conference, November 11–15, 2001, Nashville, TN, USA

EC- Official Jour, of the European Communities (1975) 18:6 (Sept. 18)

Gittelman TS & Yohe TL (1989) Treatment of the iodinated haloform medicinal odors in drinking water. Proceedings AWWA Ann. Conf., Los Angeles, Calif., USA (pp. 105–123).

Khiari D, Brenner L, Burlingame GA & Suffet IH (1992) sensory gas chromatography for evaluation of taste and odor events in drinking water. Wat. Sci. Tech. 25(2): 97–104

Khiari D, Young C, Ye Q, Amar G, Atasi K, Huddleston J & Suffet IH (1999a) Factors affecting the stability and behavior of grassy odors in drinking water. Wat. Sci. Tech 40(6): 287–292

Khiari D, Barrett SE & Suffet IH (1997) Determination of organic compounds causing decaying vegetation and septic odors in drinking water by sensory GC. Jour. AWWA 89(4): 150–161

Khiari D, Suffet IH & Barrett SE (1995a) Extraction and identification of chemicals causing grassy odors in FPA reference standards. Wat. Sci. Technol. 31(11): 93–98

Khiari D, Suffet IH & Barrett SE (1995b) The determination of compounds causing fishy/swampy odors in drinking water supplies. Wat. Sci. Technol. 31(11): 105–112

Krasner SW & Barrett SE (1984) Aroma and flavor characteristics of free chlorine and chloramines. Proceedings AWWA Wat. Qual. Technol. Conf., Denver, CO, USA

Krasner SW, McGuire MJ & Ferguson VB (1985) Tastes and odors: The flavor profile method. Jour. AWWA 77(3): 34–39

Maine DHS (Department of Human Services) (1998) Maine Department of Environmental Protection, and Maine Department of Conservation. The presence of MTBE and other gasoline compounds in Maine's drinking water, a preliminary report, October 13, 1998

Mallevialle J & Suffet IH (1987) Identification and Treatment of Tastes and Odors in Drinking Water. ISBN #0-89867-392-5. AWWA Research Foundation and Lyonnaise Des Eaux Cooperative Research Report, American Water Works Assoc., Denver, Colo., USA

Meilgaard MG, Civille GV & Car BT (1999) Sensory Evaluation Techniques, 3rd edn. CRC Press, Boca Raton, FL, USA

Neilson AJ, Ferguson VB & Kendall DA (1988) Profile methods: Flavor profile and profile attribute analysis. In Moskowitz H (Ed) Applied Sensory Analysis of Foods (II) (pp 21–41). CRC Press, Inc. Boca Raton, Fla.

Montiel A (1991) Study investigating the origin and mechanism of formation of sapid components preceding musty taste in our water supply. Proceedings AWWA Wat. Qual. Tech. Conf., Orlando, Fla., USA

Moskowitz HR, Dravnieks A, Cain WS & Turk A (1974) Standardized procedure for expressing odor intensity. Chem. Senses and Flavor 1: 235

Noblet J, Schweitzer L, Ibrahim E, Stolzenbach K, Zhou L & Suffet IH (1999) Evaluation of a taste and odor incident on the Ohio River. Wat. Sci. Technol. 40(6): 185–194

Nystrom A, Grimvall A, Krantz-Rulcker C, Savenhed R & Akerstrand K (1992) Drinking water of off-Flavor caused by 2,4,6-trichloranisole. Wat. Sci. Technol. 25(2): 241

Persson PE (1992) A summary of problem areas in aquatic off-flavor research. Wat. Sci. Technol. 25(2): 335

Pretti G, Gittelman TS, Staudte PB & Luitweiller P (1993) Letting the nose lead the way. Mal-odorous compounds in water. Anal Chem. 65: 699A–702A

Rashash DMC, Hoehn RC, Dietrich AM & Parker BC (1993) Isolation and identification of algal odor compounds by CLLE, GC/MS and FPA. Proceedings AWWA Wat. Qual. Technol. Conf., Miami, Fla., USA (pp 591–597)

Slater GP & Block VC (1983) Volatile compounds of the cyanophyceae – a review. Wat. Sci. Technol. 15(6/7): 181

Stocking I, Suffet MJ, McGuire M & Kavanaugh (1999) Implications of a MTBE Consumer Threshold Odor Study for Drinking Water Standard Setting. Jour. AWWA 93(3): 95–105

Suffet IH, Khiari D & Bruchet A (1999) The Drinking Water Taste and Odor Wheel For The Millennium: Beyond Geosmin And Methyl Isoborneol. Wat. Sci. Technol. 40(6): 1–13

Suffet IH, Mallevialle J & Kawczyski E (Ed) (1995) Advances in Taste-and-Odor Treatment and Control. AWWA Research Foundation and Lyonnaise Des Eaux Cooperative Research Report, American Water Works Assoc., Denver, Colo., USA

Suffet IH, Corado A & Khiari D (1995b) Brominated organic compounds and tastes and odors in water supplies. Wat. Suppl Jour. 13(1): 85–99

Suffet IH, Brady B, Bartels JHM, Burlingame G, Yohe TL & Mallevialle J (1988) Development of the flavor profile method into a standard method for sensory analysis of water. Wat. Sci. Technol. 20(8/9): 1

Thiemer ET (Ed) (1982) Fragrance Chemistry: The Science of the Sense of Smell. Academic Press, New York, N.Y., USA

UK Water Industry Research Ltd. (UKWIR) (1996) Formation and Occurrence of Bromophenol, Iodo-phenols, Bromoanisoles and Iodoanisoles in Drinking Water: An Investigation of Taste and Odor Potential. Report DW-05/13, UKWIR, London, UK

USEPA (1979) National Secondary Drinking Water Regulations. Final Rule. Fed Reg. 44:140:42195

USEPA (1991) National Secondary Drinking Water Regulations. Final Rule. Fed Reg. 56:20:3526

USEPA (1998) Disinfection and Disinfection Byproducts. Final Rule. Fed. Reg., 63:241:69390

USFDA (1979) Quality Standards for Food with No Identity Standards-Bottled Water. 21 CRF Part 103, 4–45, 12172

Ventura F, Matia L, Romero J, Boleda M^{a}R, Martí I & Martin L (1995) Taste and odor events in Barcelona's water supply. Wat. Sci. Technol. 31(11): 63–68

Worsley, JL, Dietrich AM & Hoehn RC (2003) Dechlorination Techniques Used to Improve Sensory Odor Testing of Geosmin and 2-MIB. Jour. AWWA 95(3): 109–117

Yano H, Nakahara M & Ito H (1988) Water blooms of *Uroglena americana* and the identification of odorous compounds. Wat. Sci. Technol. 20(8/9): 75

Young C, Suffet IH, Crozes G & Bruchet A (1999) Identification of a woody/hay odor-causing compound in a drinking water supply. Wat. Sci. Technol. 40(6): 279–285