Sensory and chemical analysis methods for earthy and musty odours in drinking water caused by geosmin and 2-methylisoborneol

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Abstract Earthy and musty odours are amongst the most frequently observed objectionable odours in water supplies, and geosmin and 2-methylisoborneol are identified as the chemical compounds most closely associated with these odours. In this paper, the sensory properties, and the water matrix effects on taste and odour panel studies, as well as the chemical analysis methods for earthy and musty odours in drinking water caused by geosmin and 2-methylisoborneol, are reviewed. Insights are developed to enable better evaluation of earthy and musty odours in drinking water. Early detection of geosmin and MIB can prevent off-flavour occurrence by providing information for potential treatment.

Keywords Chemical analysis; drinking water; earthy and musty odours; geosmin; 2-methylisoborneol; sensory properties; water matrix effects

Introduction

Objectionable tastes and odours can develop in drinking water for a variety of reasons. The principal causes tend to be algal metabolites, metabolites from microorganisms that decay organic matter, and industrial and domestic wastes. In treated or finished drinking water, the causes may be degradation of water quality in distribution systems, the use of particular disinfection chemicals, or inadequately treated raw water (Bartels and Suffet, 1986; Yohe, 1986).

Earthy or musty odours are amongst the most frequently observed objectionable odours in water supplies (Suffet et al., 1996). These earthy or musty odours may go undetected in raw and finished waters as they can be masked by stronger odours, until treatment removes the masking substances. Often, even water treatment processes may mask these odours. For example, chlorine has been known to mask earthy or musty odours in treated drinking water as the water leaves the drinking water plant (Bartels et al., 1989; Suffet et al., 1995; Worley et al., 2003). However, these earthy/musty odours may later become detectable by consumers as the masking chlorine odour is reduced within the distribution system. Earthy or musty odours may also be caused by the presence of microorganisms and their related metabolites within the distribution system (Montiel, 1991).

In raw water, geosmin and 2-methylisoborneol (MIB) have been identified as the chemical compounds most closely associated with earthy and musty odours, respectively. The odour threshold concentration of geosmin and MIB are < 10 ng/L (Mallevalle and Suffet, 1987). Geosmin and MIB have been isolated as metabolites of a variety of algae in raw drinking water supplies. It is important to note, however, that geosmin and MIB are not the only chemicals that may produce earthy or musty odours. There have been
reported instances where earthy or musty odours are detected, yet chemical analysis identified no geosmin or MIB present (Bruchet, 1999).

**Sensory properties of MIB and geosmin tastes and odours in water**

The biological and chemical origins of a variety of unfavourable odorants have been identified in drinking water supplies through a combination of various chemical and sensory analytical methods (Suffet et al., 2004). Investigations of source waters and distribution systems have revealed a wide variety of chemicals and microorganisms that contribute and cause problematic tastes and odours (Mallevalle and Suffet, 1987; Suffet et al., 1995, 2004). The methods of chemical analysis include the use of gas chromatography/mass spectrometry and sensory gas chromatography in coordination with any one of several methods of extraction best suited for the isolation of the compounds of interest. In addition to the various methods of chemical analysis, sensory panel analytical techniques, such as the flavor profile analysis (FPA), have also proved invaluable for the identification of unfavourable tastes and odours (Suffet et al., 1988).

The threshold odour number (TON) test (APHA, 2000) is a common method for the characterization of an odour intensity within a drinking water sample. This method, however, is inadequate for the characterization of odours because it provides no qualitative descriptive system, and gives an overall intensity of the odours at each dilution without identifying individual odour components. Additionally, it is not necessary that the chemical perceived in the diluted sample be the same as the chemical causing the unfavourable odour in the undiluted sample. As such, odours of lower dilution should be taken into careful consideration if they contribute to the objectionable odour of the undiluted sample. There is poor correlation between TON results and the level of acceptability of water supplies as determined by consumer evaluation (Mallevalle and Suffet, 1987).

The FPA method was first introduced as an adaptation from the food industry by the Metropolitan Water District of Southern California (Krasner et al., 1985), and has since been the source of reproducible and valid data for specific tastes and odours in drinking water (Mallevalle et al., 1984; Krasner et al., 1985; Bartels et al., 1986, 1989; Suffet et al., 1988). The Webster’s Dictionary definition of flavour is ‘that quality of a substance that is a mixing of its characteristic taste and smell’. In addition to the chemical stimulation of the taste buds, flavour also includes stimulation of the olfactory bulb in the nose and the sensory organs in the mouth and throat. While there are only four distinct tastes—sweet, sour, bitter, and salty—the number of possible flavours, combinations of tastes and odours, is practically limitless (Amoore, 1962, 1986; Amoore et al., 1964).

The pairwise ranking test (Meilgaard et al., 1999) is a sensory technique in which statistics can be used to evaluate several samples compared for a single attribute. Samples are arranged on a scale of intensity of the chosen attribute, and assigned a value indicating the differences between samples and the significance of these differences.

A crucial element in the prevention and control of taste and odour problems consists of a regular monitoring program of source and finished water. FPA is the ‘gold standard’ to be used for the early detection of taste and odour compounds by monitoring taste-and-odours in water and 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 attribute rating test, the 2-of-5 odour test, and a rating method for evaluating distribution system odours in comparison to a control (Dietrich et al., 2004a, b, c). 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 (Table 1).
Sensory testing is generally inexpensive, requires only a minimal amount of training, and has a short turn-around time when compared to chemical analysis. However, the tests must be properly designed and conducted so that accurate decisions can be made based on the results. An important consideration for any sensory test is the number of replicate samples that must be evaluated to achieve a desired degree of confidence in the results and to limit false positive and false negative conclusions (Gallagher, 2004).

<table>
<thead>
<tr>
<th>Method name</th>
<th>Features</th>
<th>Performance</th>
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| Attribute rating test | To evaluate the presence or absence of a chemical | 1. Allows for the rating of the intensity of an odorant  
2. Standard is provided at a concentration at which consumers start to complain  
3. Using a paired-comparison format  
4. The method does not currently inform utilities how to respond to the rating |
| 2-of-5 odour test | To determine noticeable differences between water samples | 1. Applies to routine monitoring of raw or finished water to detect odour changes over time and tracking odour problems in watersheds  
2. To be a forced comparison test, requiring only 1 to 5 persons with minimal training  
3. To be statistically sound  
4. It could be used to determine if a source of water really has an odour that consumers may notice |
| Rating method for evaluating distribution-system odours | For evaluating distribution system odours in comparison to a control | 1. Compares the difference between a control water and distribution system water  
2. Requires one test administrator and two panelists  
3. To be much like FPA  
4. To be easier but less precise than FPA |

*From Suffet et al., 2004

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**Threshold, water matrix effects on geosmin and 2-methyl isoborneol**

Geosmin and MIB are known to be metabolites of certain blue-green algae (*cyanobacteria*) and *actinomycetes* and persistently appear in the spring and summer (Mallevialle and Suffet, 1987). Massive growths of benthic cyanobacteria in rivers may produce large concentrations of geosmin in the water (Vilalta et al., 2003), causing poor water quality and consumer complaints. Although the relationships existing between the number of microorganisms and odour intensity are not completely understood, typically, elevated levels of these compounds are present when the producing organism is found in abundance. This is frequently associated with high nutrient levels, warm water, and calm weather. Only chemical analysis of the drinking water can prove that geosmin or MIB is the cause of the taste-and-odour problem.

Geosmin and MIB fall into the dubious category of compounds that can be detected more easily by the human nose than by conventional laboratory techniques. Therefore, odour panels have been used as an inexpensive early warning system to signal a taste and odour event (Means and McGuire, 1986). A combination of odorants can interfere with the identification of individual odorants. Some chemicals can mask other odours (serving as antagonists), or act synergistically to make the odours seem stronger than what
the intensities would be if present individually. Also, a chemical’s odour characteristics may change as a function of concentration, or may change for other reasons (Suffet et al., 2004). For example, in water distribution systems, trichlorophenols, which are chlorination by-products, can be transformed to trichloranisoles, and musty odours occur via the methylation process (Montiel, 1991). Free chlorine odour has the ability to mask earthy and musty odours, and this is one of the reasons earthy and musty odours are better detected when chlorine levels are lower (Worley et al., 2003).

Residual chlorine can also affect the analysis of geosmin and MIB in water. The presence of chlorine substantially reduces the observed geosmin and MIB concentrations when using SPME-GC/MS (Lin et al., 2003). In another report by Oestman et al. (2004), the effects of chlorine and chloramines on earthy and musty odours in drinking water were evaluated by two sensory analysis approaches, a statistical pairwise comparison test, and FPA. The results show that panelists can differentiate minor differences in geosmin and MIB concentrations in a pairwise comparison test even in the presence of chlorine. FPA appeared to be more challenging in discerning subtle differences in concentrations of geosmin or MIB than did the pairwise comparison test, and the presence of chlorine (0.5–20 mg/L) and chloramines (3–24 mg/L) confused the panelists (i.e. showed a larger error in the intensity of response reported by the panel), but did not necessarily mask geosmin or MIB.

Odour analyses experiments indicated that, for the concentrations and temperatures tested, odour intensity was a function of both aqueous concentration and water temperature for water containing geosmin and MIB. At weak odorant concentrations (approximately 4 on the flavour profile rating scale), the perceived odour intensity of geosmin and MIB was greater when the temperature was 45 °C than when it was 25 °C (Whelton and Dietrich, 2004).

Reported odour threshold concentrations for MIB and geosmin vary significantly. First, there has been considerable error associated with quantifying MIB and geosmin at the very low levels required to approach the thresholds (i.e. 1 to 10 ng/L), as analytical methods developed (Suffet et al., 1995). In one report, consumer complaints tended to increase significantly when MIB concentrations were 10 to 15 ng/L or greater (Krasner et al., 1985). The odour threshold concentrations for MIB and geosmin are generally summarized to be in the range of 5 to 10 ng/L (Suffet et al., 1995). The geometric means of the odour threshold concentrations of geosmin and MIB are reported by Young et al. (1996) to be 3.8 ng/L and 15 ng/L, respectively. It must be remembered that the odour threshold concentration is the median value of the population tested. It is not the lowest value detected by the most sensitive individuals of the population. Thus, some people will detect MIB and geosmin at concentrations below 5 ng/L.

Chemical analysis methods for monitoring and detection of MIB and geosmin in water

Sensory analysis has been found effective for the detection of known taste- and odour-causing compounds at the nanogram-per-litre levels. Thus, chemical analysis of trace organic compounds in water requires a very sensitive analytical procedure because of the low concentrations at which these organic compounds occur in water. Besides a low detection level, the analytical method also requires a high discriminatory capability because of the amount of different organic contaminants commonly present in samples. The method most suitable for detection of organic compounds is capillary gas chromatography-mass spectrometry (GC-MS).

Often, the most challenging step for the analytical chemist is to attribute the overall odour of the water sample to specific chemicals. The best approach is to use
a sensory-GC technique, which was first described by Fuller et al. in 1964 (Fuller et al., 1964). By using sensory-GC technique, the effluent of the gas-chromatography column is divided into two parts; the first portion is sent to a GC detector while the second goes to an olfactory port and is smelled by a trained operator. The technique was tested with standard compounds and applied to real cases of taste and odour episode by Hochereau and Bruchet (2004). This approach allowed the identification of geosmin and MIB at low levels. The compared detection limits by GC-Sniff and GC-MS are listed in Table 2.

GC/MS methods can be used only after the compounds of interest are isolated from the water phase and concentrated in a second phase. In addition to recovering the odorous compounds present in the water sample, the isolation technique chosen should not modify the organic compounds. In real situations, however, these requirements can only be approximated. Several techniques are available for isolation of the compound. Closed-loop stripping analysis (CLSA), a standard method for geosmin and MIB, is based on the stripping of semi-volatile organics by an inert gas from the water. With continuous liquid–liquid extraction (CLLE), lipophilic organics are extracted from the water with a suitable organic solvent. In general, this has to be followed by a concentration step, such as Kuderna-Danish (K–D) distillation. Steam distillation extraction (SDE) is a gas phase liquid–liquid extraction under reflux conditions. Another approach is the isolation of the chemicals onto resins, after which elution and K–D distillation are necessary. The newest standard method (APHA, 2000) for isolation of odorants, especially for geosmin and MIB, is solid phase micro-extraction (SPME). SPME isolates the chemicals on a coated fibre. Based on SPME fibre, a new approach using stir bars coated with PDMS (polydimethylsiloxane) was developed recently for analysing the taste and odour compounds, including geosmin and MIB, in raw and drinking water (Nakamura et al., 2001; Benanou et al., 2003). In this approach, 50–300 μL PDMS coatings are used. Consequently, sensitivity is increased by a factor of 100 to 1 000. Complete recovery is possible for solutes with k (o/w) larger than 500. Solutes with k (o/w) from 10 to 500 can also be analysed using calibration, as is done in SPME. This technique is called stir bar sorptive extraction (SBSE).

Closed loop stripping analysis (CLSA) was widely used for the analysis of nonpolar, volatile organic compounds of intermediate molecular weights at parts-per-trillion to parts-per-billion levels in the 1990s. Using CLSA for extraction followed by GC-MS, a method applicable to both treated and natural waters, trace organics are detectable at nanogram-per-litre levels. A standardized GC-MS method has been developed especially for the isolation of MIB and geosmin by Krasner and co-workers (Krasner et al., 1981, 1983), based on the method of Grob (Grob and Zurcher, 1976). This method was developed as a standard method specifically for the isolation of earthy–musty taste- and odour-causing compounds (APHA, 2000). At present, CLSA is used primarily as a broad spectrum analysis for volatile compounds causing odours in water with sensory GC and GC/MS identifications (Khiari et al., 1992).

An alternative method, steam distillation extraction (SDE), was originally developed as a second broad spectrum analysis method because of its widespread use in the analysis of food odours (Buttery et al., 1976; Gavinelli et al., 1986). SDE was found to be more

<table>
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<tr>
<th>Table 2</th>
<th>Compared detection limits by GC-Sniff and GC-MS*</th>
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<tr>
<td><strong>Standard</strong></td>
<td><strong>Detection limit by GC/MS (full scan)</strong></td>
</tr>
<tr>
<td>MIB</td>
<td>2 ng/L</td>
</tr>
<tr>
<td>Geosmin</td>
<td>2 ng/L</td>
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</tbody>
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*From Hochereau and Bruchet, 2004
effective than CLSA in the collection and isolation of compounds with higher molecular weights and higher polarities (Mallevialle et al., 1984). Used in conjunction with CLSA, SDE can provide more knowledge on taste- and odour-causing compounds in drinking water because SDE widens the range of less volatile contaminants that can be detected. SDE is used primarily as a supplement to CLSA in order to increase the ability to determine the causes of unknown organoleptic problems.

The most widely used standard method for concentrating MIB and geosmin from water in recent years is the SPME technique (APHA, 2000). SPME-GC/MS has been used widely in the analysis of many organic compounds in water, including taste and odour compounds, during the past several years (Mindrup and Shirey, 1998; Watson et al., 2000; Zimmerman et al., 2002). This method has many advantages over the conventional methods of CLSA for analysing geosmin and MIB in water. Detection limits are comparable to those obtained with CLSA, but SPME is much simpler, less labour and time intensive. Smaller volumes of samples are required. It does not require a solvent and it is relatively inexpensive to set up and run. In addition, the method has the potential for automation, which further increases sample throughput and decreases analysis costs.

Although there has been success at characterizing water both chemically and organoleptically, there is, at present, less comprehensive and generalized methods for integrating data obtained from chemical and sensory analyses. Mallevialle and Suffet (1987) introduced background information on chemical/sensory correlation methods and showed general results from correlation studies. A case study was presented in which a method was offered for statistically relating chromatographic and organoleptic data. The study demonstrated the feasibility of developing a predictive model that allows the organoleptic characteristics of water to be obtained from instrumental data (Bartels and Suffet, 1986). Suffet et al. (1989) used a similar statistical method, factorial correspondence analysis, to correlate chemical and sensory data. A statistical method utilizing principal component factor analysis (PCFA) was developed for chemical/sensory taste and odour correlation by Meng and Suffet (1997). With this method, specific flavour descriptors can be correlated with specific chromatographic peaks.

**Results and discussion**

Figure 1 shows that to determine the chemical causes of taste and odour problems requires developing a presumptive statistical correlation between the chemical compounds in the water sample and the tastes or odours 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 and by sensory-GC analysis (Khiari et al.,

![Figure 1](https://iwaponline.com/ws/article-pdf/6/3/147/418192/147.pdf)
Figure 1 shows that final confirmation is completed by having the sensory panels evaluate the chemical identified by FPA and sensory-GC.

Figure 1 also presents the key relationship between odour panel analysis by FPA, chemical identification by GC/MS and sensory-GC to identify the odorous chemicals in the chemical mixture presented by GC/MS. Confirmation of the analysis occurs when the compounds identified by GC sensory analysis are added to water and confirmed to smell similar to the original odours water.

Conclusions
Earthly and musty odours are amongst the most frequently observed objectionable odours in water supplies, and geosmin and 2-methylisoborneol have been identified as the chemical compounds most closely associated with these odours. In this paper, the sensory properties, and the water matrix effects on taste and odour panel studies, as well as the chemical analysis methods for earthy and musty odours in drinking water caused by geosmin and 2-methylisoborneol, are reviewed. Insights are developed to enable better evaluation of earthy and musty odours in drinking water. There are numerous earthy and musty odour episodes or cases that cause consumer complaints in many countries (Izaguirre et al., 1982; Burlingame et al., 1986; Yagi, 1988; Izaguirre and Taylor, 1995; Bruchet, 1999; Davies et al., 2004; Fabrellas et al., 2004). Early detection of geosmin and MIB can prevent off-flavour occurrence by providing information for potential treatment. Sensory and chemical methods provide comprehensive analysis approaches of taste and odour chemicals in every stage of drinking water supplies.

References


