Wat. Sci. Tech. Vol. 20, No. 8/9, pp. 11–17, 1988.
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0273–1223/88 $0·00 + ·50
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THE RELATIONSHIP BETWEEN CONCENTRATION AND SENSORY PROPERTIES OF 2-METHYLISOBORNEOL AND GEOSMIN IN DRINKING WATER

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ABSTRACT

The study of the relations between the senses of smell and taste and odorant concentration is important for the solution of odor problems. The threshold concentrations of odor and taste (TOC, TTC) of 2-methylisoborneol (MIB) and geosmin were measured by the non-forced choice triangle method using 12-20 panelists. Both TOC and TTC were found to be functions of water temperature and the concentration of residual chlorine. The TOC and TTC of mixed samples were rather lower than the concentrations calculated from the mixing ratio. The sensitivities of the consumer panel and the number of musty odor complaints from consumers are related to MIB or geosmin concentration. The ratio of the number of complaints to MIB (or geosmin) concentration decreased after maximum complaint, but the sensitivity of the consumer panel remained the same.

KEYWORDS

2-methylisoborneol, geosmin, sensory test, drinking water, complaint, consumer panel.

INTRODUCTION

Consumer satisfaction with tap water is sharply decreased by musty odor problems. To solve these problems, it is necessary to understand the relations between odorant concentrations and their sensory properties. There is no relation between threshold odor number (TON) and 2-methylisoborneol (MIB) concentration (Ito, 1984). Persson (1980) reported that the threshold odor concentrations (TOCs) of MIB and geosmin ranged over wide concentrations, so more detailed information is needed to establish the guideline values of MIB and geosmin for drinking water. TOC and TTC are influenced by several factors. Concerning TTC, Pangborn (1970) reported the influence of minerals, and discussed the effects of temperature (Pangborn, 1972), while Bryan (1973) demonstrated the importance of pH. Concerning the TOC of MIB and geosmin, Nishida (1985) reported the influence of water temperature and the relevance of residual chlorine. However,

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detailed knowledge of the TOCs and TTCs of MIB and geosmin still needs to be clarified. We have embarked on an investigation consisting of three tests, two of which, a laboratory panel (expert panel) test and a consumer panel test, were carried out in the manner described by de Greef (1983). To these tests we have added a survey of the number of consumer complaints.

OUTLINE OF WATERWO KS OF OSAKA PREFECTURE

The Osaka Prefectural Waterworks (OPWW) treats flow water of Yodo River, which consists of 3 main rivers, the Kizu, the Katsura and the Uji, this last originating in Lake Biwa. The Yodo runs through the Kyoto-Osaka area and the treated water supplies 13 million consumers in the Kyoto-Osaka-Kobe region. About 70% of the water in the Yodo runs out from Lake Biwa. In 1969, a musty odor was detected in Lake Biwa, and since 1970, this odor has often been found in the waters of the Yodo. Kikuchi (1973) identified MIB and geosmin in Lake Biwa as the musty odor compounds. OPWW removes this musty odor by adding powdered activated carbon (PAC), but in addition to the high cost of PAC, it is difficult to determine to what extent musty odorant concentrations can be eliminated. The same problem occurs in the case of high level treatment with ozone, granular activated carbon and biofilm. The OPWW drinking water supply system consists of two treatment plants, Murano and Niwakubo, which distribute 1.8 and 0.14 million m^3/day respectively. Their distribution areas have almost no overlap, but the treatment techniques are the same, namely, PAC, break point chlorination, coagulation, sedimentation, sand filtration and postchlorination.

METHODS

<u>Laboratory panel test.</u> TOC and TTC were measured according to the official Japanese method of measurement for TON of offensive atmospheric odor (Environmental Agency of Japan, 1982). This official method is by non-forced choice triangle test using 6 panelists, with the threshold odors calculated after eliminating the highest and the lowest scoring panelists. In this investigation, TOC and TTC were measured in ascending order by the non-forced choice triangle test, and were calculated as follows:

$$X = \frac{1}{n}\sum\left(\log(\sqrt{C_{i1}} \times \sqrt{C_{i2}})\right)$$

$$TOC(TTC) = 10^X$$

where:

C_{i1} = the lowest correct concentration of panelists i,
C_{i2} = the highest incorrect or no-reply concentration of panelists i,
n = the number of panelists after eliminating the same number of high and low scoring panelists.

The number of panelists ranged between 12 and 20. The panelists were members of the OPWW Water Testing Station, and were familiar with both musty odor and TON test. MIB and geosmin were obtained commercially from Wako Pure Chemical Ind. Ltd (Osaka, Japan). MIB and geosmin concentrations were determined by the stripping GC/MS

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method (Ito, 1983). Odor- and taste-free water was prepared by boiling pure water (Millipore Co.) and distilled water. For TOC measurements, the panelists sniffed 200ml samples, after shaking, in 300ml wide-necked glass bottles with glass stoppers. For TTC, the panelists tasted or drank the samples in beakers. The panelists were required to choose (1) the concentration level just perceptible when compared with the odor- and taste-free water (detection TOC = DTOC) and (2) the concentration level immediately noticeable without comparison with the odor- and taste-free water (noticeable TOC = NTOC). These represent the thresholds of the laboratory panel and the consumer panel respectively. The samples were prepared at three temperatures (15, 25, 35°C) and at three free chlorine concentrations (0, 0.6, 1.5mg/l) using sodium hypochlorite.

Consumer panel test. About 200 panelists were selected to judge the taste of home tap water without comparison with the odor- and taste-free water. All panelists were housewives and lived in the area served by the Murano treatment plant. Their ages ranged between the late teens to the 60's. The object and method of the test were explained, and questions about related matters were asked before the test. The test cards were mailed 2-6 times/month between June 20th and October 27th in 1986, each panelist receiving a total of 15 cards. During the testing period, the musty odor of MIB occurred from September to October, and the number of cards mailed per month was increased.

Complaints. OPWW, in the process of distributing drinking water to 4.2 million people, has been listing complaints of musty odor from consumers daily in each city served.

RESULTS AND DISCUSSION

TABLE 1 Detection Threshold Concentrations of MIB (ng/l)

		free residual chlorine (mg/l)		
		0	0.6	1.5
15°C	DTOC	5	11	14
	DTTC	9	20	17
25°C	DTOC	5	8	11
	DTTC	7	13	17
35°C	DTOC	4	7	11
	DTTC	7	8	18

TABLE 2 Noticeable Threshold Concentrations of MIB (ng/l)

		free residual chlorine (mg/l)		
		0	0.6	1.5
15°C	NTOC	33	44	48
	NTTC	38	48	38
25°C	NTOC	24	37	45
	NTTC	27	41	42
35°C	NTOC	8	27	46
	NTTC	17	32	56

TABLE 3 Detection Threshold Concentrations of Geosmin(ng/l)

		free residual chlorine (mg/l)		
		0	0.6	1.5
15°C	DTOC	55	55	164
	DTTC	180	163	254
25°C	DTOC	33	48	76
	DTTC	139	215	159
35°C	DTOC	22	35	29
	DTTC	58	134	117

TABLE 4 Noticeable Threshold Concentrations of Geosmin(ng/l)

		free residual chlorine (mg/l)		
		0	0.6	1.5
15°C	NTOC	135	175	343
	NTTC	459	477	600
25°C	NTOC	86	100	162
	NTTC	339	365	297
35°C	NTOC	47	82	67
	NTTC	179	301	319

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Laboratory panel test. TOC and TTC of MIB and geosmin are listed in Tables 1-4. The DTOC of MIB (25°C, 0mg-Cl/l) is nearly equal to the concentration which is common TOC for this compound in Japan (5ng/l, Japan Waterworks Association, 1979), but the DTOC of geosmin is higher than the common TOC (10ng/l). In the case of MIB, the TOC is almost the same as the TTC, while the TTC of geosmin is rather higher than the TOC. The NTOC/DTOC of MIB is higher than that of geosmin, so from the point of the sensory test, the removal of MIB odor is more difficult than geosmin. The TOC and TTC of MIB and geosmin are described by the functions of water temperature and free chlorine as follows:

$$DTOC(MIB) = 4.8 \times Cl - 0.13 \times T + 8.2$$
$$NTOC(MIB) = 14.4 \times Cl - 0.65 \times T + 40.5$$
$$DTTC(MIB) = 6.1 \times Cl - 0.22 \times T + 14.1$$
$$NTTC(MIB) = 8.9 \times Cl - 0.00 \times T + 31.1$$
$$DTOC(Geosmin) = 35.7 \times Cl - 3.13 \times T + 111$$
$$NTOC(Geosmin) = 67.4 \times Cl - 7.59 \times T + 276$$
$$DTTC(Geosmin) = 28.5 \times Cl - 4.79 \times T + 259$$
$$NTTC(Geosmin) = 49.0 \times Cl - 12.3 \times T + 645$$

where:
Cl: residual free chlorine,
T : water temperature,

The TOC and TTC of the samples prepared by mixing MIB and geosmin are considerably lower than the concentrations expected when there is no interaction (Fig.1). When geosmin is the main odorant, the NTOC becomes one-half, when comparing the coexisting MIB concentration of 0ng/l with that of 5ng/l. In order to treat the musty odor problem quantitatively, a more sensitive analytical method is necessary.

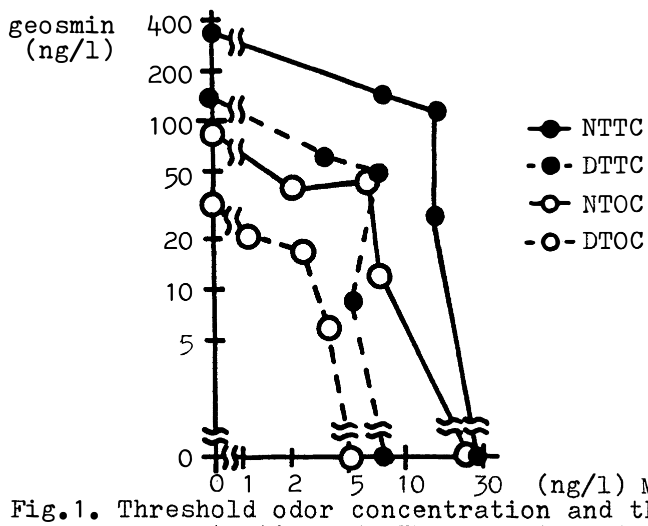

Fig.1. Threshold odor concentration and threshold taste concentration of MIB, geosmin and the mixture.

Consumer panel test. The responses were 92% at first, decreasing to 68% at the end, with an average of about 80%. The relation between MIB concentration and per cent of panelists who tasted a musty odor is shown in Fig.2. The MIB concentration at which half the panelists tasted a musty odor is extrapolated to 110ng/l.

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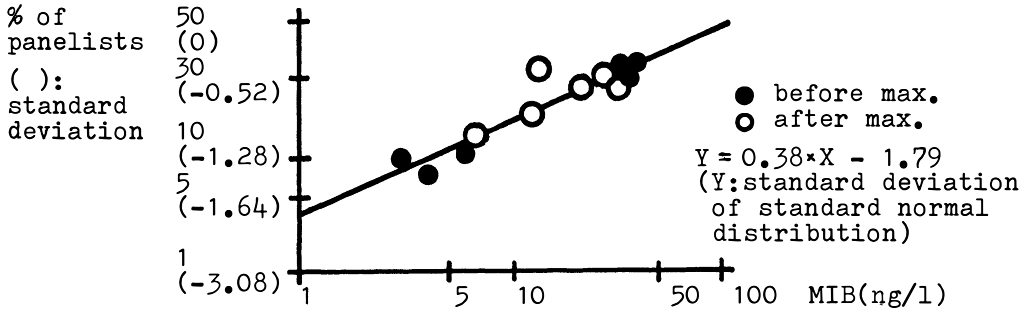

Fig.2. Relation between MIB concentration and per cent of panelists who tasted a musty odor.

This concentration is rather high compared with the TOC values reported by Persson (1980). Zoeteman (1980) reported that 5% of the population could taste or smell 1% of the threshold value, and the relation could be applied to this test. The reasons why the 50% value correlates with a high concentration may be the differences between (1) tasting 'a musty odor' and 'hardly offensive', (2) the concentration of residual chlorine, and (3) the environment.

Complaints. The relation between the number of complaints and MIB and geosmin concentration in drinking water is shown in Fig.3 and 4. The geosmin data are from August to September in 1985, the only occurrence of this compound.The MIB data have been gathered since 1985. The distribution of MIB concentration, at some complaint numbers, is logarithmic, but the normal correlation coefficient is high because high concentration data were few. The days when the complaints were made are displaced forward two days for MIB and one day for geosmin for the following reason. There is a lag between the time when MIB or geosmin concentrations were determined after processing at the Murano treatment plant and the time when the

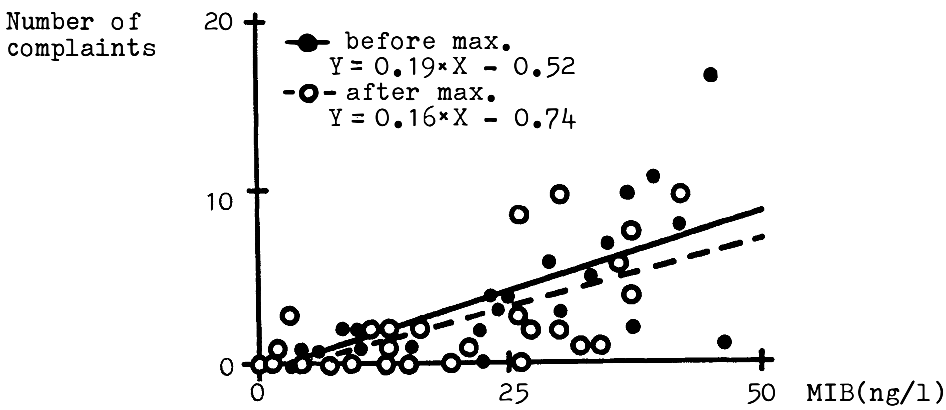

Fig.3. Relation between the number of complaints and MIB concentration

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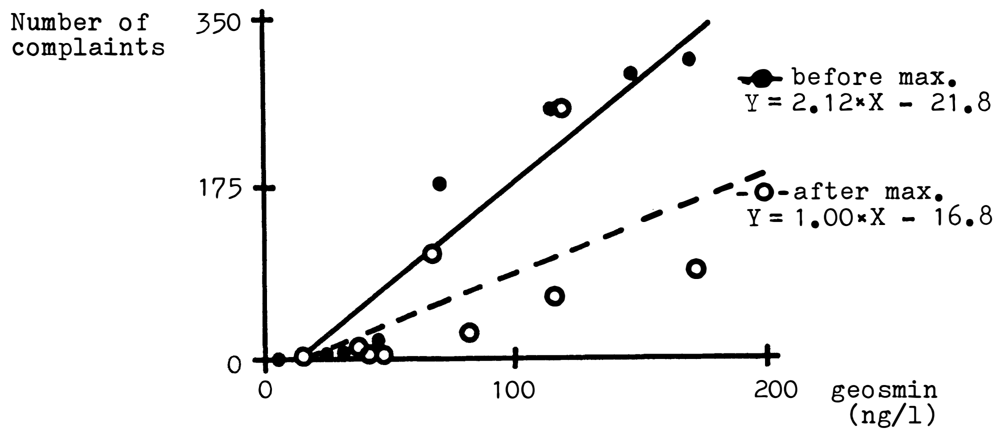

Fig.4. Relation between the number of complaints and geosmin concentration

complaints were made. The lag days were determined by finding the highest correlation coefficients between MIB or geosmin concentrations. In the case of geosmin, consumer response was very quick because the concentration peak was very sharp; consequently, the lag was only distribution time. In the case of MIB, psychological time seemed to be added, because the concentration peaks were flat.

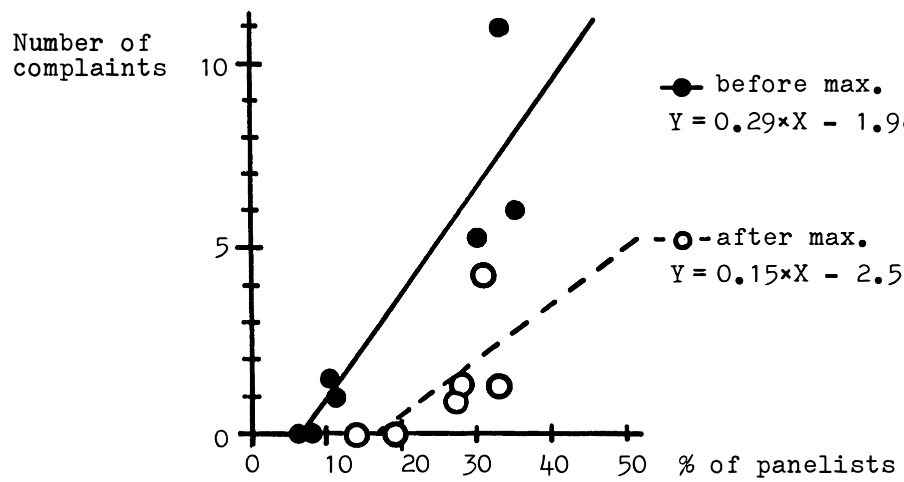

Fig.5. Relation between per cent of panelists who tasted a musty odor and number of complaints (Both of them are mean values of three days since the test cards were mailed)

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In the case of MIB, some complaints were made under 10ng/l, but for geosmin, the number of complaints increased from about 30ng/l. MIB, forwhich TOC is low and NTOC/DTOC is high, caused complaints at low concentrations and geosmin caused complaints to rise steeply at high concentrations. The regression coefficients (complaint numbers vs MIB or geosmin concentration) were different before and after the maximum complaint numbers. In the case of MIB, they are 0.19 and 0.16, and for geosmin, 2.12 and 1.00, respectively. These facts show that a kind of 'acclimation' occurred to the sensitivity of consumers as expressed in their complaints. The relation between the sensitivity of the consumer panel and the number of complaints per day is shown in Fig.5.

The number of complaints at the early period of the peak was greater than at the end. These facts mean that 'acclimation' occurred to the sensitivity of consumers who registered complaints, but it did not occur to the sensitivity of individual consumer panelists.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the advice of Prof. I. Somiya on the consumer panel test.

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