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# Gamma-Rays Treatment of Odorous Compound in Water

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**Synopsis.** $\gamma$-Rays treatment of earthy odors in public water supplies due to the metabolites in Lake Biwa was studied. The odorous compound was isolated from the metabolites and was identified to be geosmin by the use of gas chromatograph-mass spectrometer. The effect of additives and competition reaction with *p*-nitroso-*N*,*N*-dimethylaniline revealed that geosmin is decomposed effectively by hydroxyl radical produced by the radiolysis of water.

Recently, mustry and earthy odors in public water supplies have become a serious social problem.[1,2] Although attempts have been carried out to remove the odors, no satisfactory method has been developed. Activated carbon can remove some of the odors, but it is expensive and the adoption of this method is restricted to water plants of large municipalities. Chlorine has proved to be useful for removing the odors, but it intensifies some odors, particularly the musty-earthy odor of bluegreens. In comparison with these methods, treatment by ionizing radiation is more promising since the radiolysis product of water is known to effectively decompose trace constituents present in dilute solution[3-8] and chemical application of radiation sources is expected to become advantageous with the increase in the use of atomic energy, through it is expensive at present.

## Experimental

*Separation and Identification of Odorous Metabolites of Actinomyces Biwako-C Strain.* Biwako-C strain was obtained from the Murano purification plant. It was inoculated on Romano agar medium.[9] The medium was incubated with a spore suspension prepared from a slant agar medium of the organism, and the culture flasks were incubated at 28 °C for 8 days with shaking. The shaken cultures (10 liters) thus obtained were distilled and the distillate was extracted with methylene chloride. After being dried, the methylene chloride solution was carefully evaporated, giving a small amount of earthy-smelling oil.

Gas chromatography (GC) was carried out on a 20% SE-30 column (glass tube 2 m × 3 mm i.d., on 60—80 mesh chromosorb W) with a Shimadzu gas chromatograph (Model GC-5A). Temperature was raised from 100 to 220 °C at 5 °C/min. Nitrogen (40 ml/min) was used as a carrier gas. Gas-mass spectrum (GC-MS) was measured with a Shimadzu gas chromatograph-mass spectrometer (Model LKB 9000). A column of 3% SE-30 (glass tube 2 m × 3 mm i.d., on 60—80 mesh chromosorb W) was used for the measurement. Temperatures of the column and ion source were 150 and 230 °C, respectively.

*Irradiation Procedures and Analysis.* All chemical reagents were of analytical grade. Aqueous solutions were bubbled with Argon for 40 min. prior to irradiation. Oxygen and nitrous oxide were added to the solution by bubbling for 40 min. Irradiation was carried out with $^{60}$Co $\gamma$-rays (10000 Ci) at room temperature. The extracts were concentrated in a water bath (30 °C) and then analyzed on a gas chromatograph. After $\gamma$-irradiation the odor compound was extracted with methylene chloride from the aqueous solution and was analyzed quantitatively with a gas chromatograph with use of bibenzyl as an internal standard. Threshold odor tests (TO test)[10] following the standard method were carried out in order to confirm the removal of the odors and to compare this treatment with other methods.

## Results and Discussion

*Identification of the Odor Substances.* Biwako-C strain produces a strong earthy odor on liquid cultures with Romano agar medium. The odor metabolite was isolated from the culture as follows. It was distilled at 100°C and the distillate was extracted with dichloromethane. The solution was then evaporated carefully under a slightly reduced pressure. After the evaporation of dichloromethane, a scarcely volatile and oily substance with a strong earthy odor was obtained. In order to identify the isolated odor substance, we measured its gas chromatograph spectra with use of the temperature raising attachment. The spectrum has several peaks except those due to solvent, the peak at the retention time of 17 min. being the main one. The retention time is the same as that of geosmin(I).[11] The spectrum


(I)

of geosmin is measured under the same conditions as for the odor substance. The result suggests that the odor substance is ascribed to geosmin. For the sake of confirmation the mass spectrum of the compound was measured with a gas chromatograph-mass spectrometer and compared with that of geosmin. The parent peak is *m/e* 182 and the highest one *m/e* 112. The mass pattern is similar to that of geosmin. These results unambiguously indicate that the odor substance produced by Biwako-C strain, which is found in the raw water of public water supplies, can be identified as geosmin. Geosmin is thus the origin of the objectionable odor of the public water supplies.

*The Effect of $\gamma$-Irradiation.* In order to examine the effect of $\gamma$-irradiation for the removal of the odors we adopted a model system-water solutions containing a given concentration of synthesized geosmin. Table 1 gives the values of threshold odor (TO) treated by $\gamma$-irradiation of the odorous water with various doses as well as those treated with activated carbon. It is seen that the initial concentration of odor substances, 100, 200, and 400, decreases. The values were determined by the Standard Method for Water Quality. $\gamma$-irradiation to a total dose as low as $8.5 \times 10^2$ rads is enough to reduce the TO value of the water to the value obtained by carbon treatment (concentration of 50 ppm) for 30

Table 1. Threshold odor reduction of artificially produced odorous water upon exposure to γ-irradiation

| Sample | Threshold Odor[a] | | | | | |
|---|---|---|---|---|---|---|
| | Original | Activated Carbon | | γ-Irradiation (total dose)[b] | | |
| | | 10 ppm | 50 ppm | $8.5\times10^{2}$ rads | $2.5\times10^{3}$ rads | $8.3\times10^{3}$ rads |
| A | 100[c] | 40 | 10 | 18 | 10 | 5 |
| B | 200 | 61 | 14 | 20 | 10 | 5 |
| C | 400 | 91 | 30 | 22 | 10 | 5 |

a) Threshold odor was determined by the Standard Method for Water Quality. b) Dose rates are $5.1\times10^{3}$ rad/h, $1.5\times10^{4}$ rad/h, $5.0\times10^{4}$ rad/h. c) Concentration of geosmin is 1 ppb.

min. The result suggests that γ-irradiation is effective for the reduction of the odor.

*Mechanism of the Reduction of the Odor.* Although the real system of water supply is not so simple as the model system we adopted, a study of the decomposition process of the synthesized geosmin in distilled water is indispensable to reveal the fundamental mechanism of the reduction of the odor. Figure 1 shows the destruction of geosmin in water by γ-irradiation with various doses. The concentration of geosmin was determined by gas chromatography with the use of bibenzyl as an internal standard. 1 mg geosmin in 1 liter water undergoes almost completely decomposition giving a value less than the least detectable one by γ-irradiation to a total dose of $5.0\times10^{4}$ rads with a dose rate of $3.0\times10^{4}$ rad/h. The dependence of the rate of destruction on the dose rate is shown in Fig. 2. The slope is 0.62. The value suggests that destruction is caused by the intermediates, which disappear by second order reaction, probably by radicals. In order to confirm this radical mechanism, the effect of additives is examined. Addition of ethanol (0.02 M), a good hydroxyl radical scavenger, decreases the *G*-value, though the addition of $N_2O$, which is a hydrated electron scavenger, increases it. The results indicate that the destruction of geosmin is caused by radicals, especially by hydroxyl radical produced by the radiolysis of water.

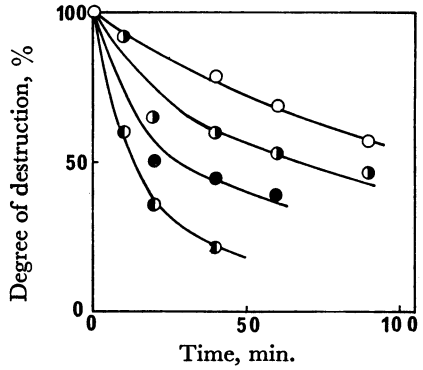


Fig. 1. Destruction of a 1 mg/l geosmin solution. Dose rates are
(○) $2.6\times10^{3}$ rad/h, (◑) $5.0\times10^{3}$ rad/h, (●) $1.1\times10^{4}$ rad/h, (◐) $3.0\times10^{4}$ rad/h.

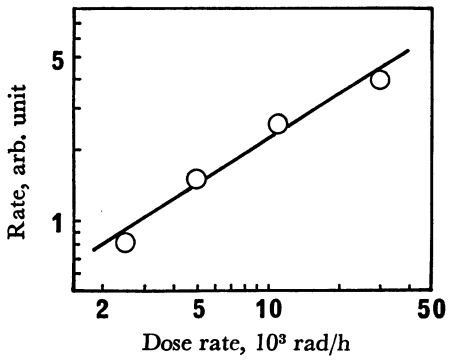


Fig. 2. Dependence of the rate of destruction on the dose rate.

The rate constant of the reaction of OH radicals with geosmin, which is considered to be the primary step for removal of the odors, is determined by competition kinetics using *p*-nitroso-*N,N*-dimethylaniline[12] as follows.

$$\mathrm{OH} + \mathrm{PNDA} \xrightarrow{k_1} \text{Product}$$

$$\mathrm{OH} + \text{geosmin} \xrightarrow{k_2} \text{Product}$$

where PNDA is *p*-nitroso-*N,N*-dimethylaniline. The decrease of PNDA determined by absorption spectra at 440 nm is expressed by

$$\frac{1}{G(-\mathrm{PNDA})} = \frac{1}{G(\mathrm{OH})}\left\{1+\frac{k_2(\text{geosmin})}{k_1(\mathrm{PNDA})}\right\}$$

The relation between $1/G(-\mathrm{PNDA})$ and (geosmin)/(PNDA) is linear. From the slope the $k_2$ value of $6.5\times10^{9}$ $M^{-1}s^{-1}$ is obtained with use of the $k_1$ value of $1.1\times10^{11}$ $M^{-1}s^{-1}$.[13] The $k$ value is slightly higher than that of ethanol and phenol. The high $k$ value also confirms the fact that the odor is easily decomposed by γ-irradiation.

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