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Note

Determination of geosmin in water by computer-controlled mass fragmentography

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Geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) is a compound with a musty odour that is a metabolite of some kinds of actinomyces¹⁻⁴. A musty odour occurs in water from polluted rivers and lakes in Japan, and Kikuchi and co-workers^{5,6} isolated actinomyces from some lakes and, after cultivation, detected geosmin in the culture medium by gas chromatography-mass spectrometry. Quantification by means of gas chromatography, however, is very difficult, because the concentration of geosmin in water is extremely low in comparison with other organic compounds. The odour threshold of geosmin in water is *ca.* 10 ppt*. As the amount of geosmin producing a musty odour in water can be used to indicate the extent of water pollution, the establishment of an accurate trace method for the determination of geosmin is very important.

Gas chromatography-mass fragmentography is a very selective and sensitive method for detecting geosmin without interfering with other components. This paper describes a quantitative method for the determination of geosmin in water using computer-controlled mass fragmentography.

EXPERIMENTAL

Standard aqueous solution of geosmin for recovery test

A suitable volume of an acetone solution of geosmin (1 µg/ml) was added to tap water (1 l) which did not contain geosmin, and 5 and 0.5 ppb solutions were prepared.

Extraction of geosmin from water

A water sample (1 l) was extracted with dichloromethane (50 ml) after dissolution of sodium chloride (300 g). The extracted solution was dried for several hours over anhydrous sodium sulphate (15 g), then concentrated to several hundred microlitres using a Kuderna-Danish concentrator under atmospheric pressure.

* Throughout this article, the American trillion (10¹²) and billion (10⁹) are meant.

Gas chromatography

A 1 m \times 2 mm I.D. column packed with 1% OV-1 on Chromosorb W (80–100 mesh) was used. The column temperature was 100°, the injection port temperature 250° and the carrier gas was helium at a flow-rate of 40 ml/min (3 kg/cm²).

Computer-controlled mass fragmentography

A JEOL Model JMS-D 100 mass spectrometer was connected with a JEOL Model JGC-20K gas chromatograph and a JEOL Model JMA-2000 mass data analysis system. The mass spectrometer has a double-focussing system and was operated with a resolution (10% valley) of *ca.* 1000. The magnetic field was set at *m/e* 104 and the accelerating voltage was changed at intervals of 0.3 sec. Repetition of a small range sweep (2 mass units) on each mass number setting (105, 112) was carried out for the correction of deviations of the magnetic field.

RESULTS AND DISCUSSION

Geosmin shows a base peak at *m/e* 112, whereas organic substances that were present in geosmin-free river water did not show a peak at *m/e* 112 in the mass fragmentogram under the conditions used. As the dynamic range in the mass spectrometer is very narrow and injection of an exact volume with a microsyringe is not sufficiently accurate, quantitative analysis was carried out using an internal standard method. *n*-Butyl benzoate was selected as the internal standard, as the retention times of geosmin and *n*-butyl benzoate in the gas chromatogram were similar and a base peak at *m/e* 105 in the mass spectrum of *n*-butyl benzoate was near to the *m/e* 112 peak of geosmin. *n*-Butyl benzoate in hexane solution was added to a hexane or dichloromethane solution of geosmin at a rate of 1 μ g per 1 ml of solution.

A calibration graph (Fig. 1) was prepared using the ratio of the peak areas of geosmin and *n*-butyl benzoate. The detection limit of geosmin was 10 ng/ml, but a more reliable value was over 50 ng/ml. An example of a mass fragmentogram is shown in Fig. 2. The precision of measurement was obtained by making measurements on the same sample five times. The results are shown in Table I. The coefficient of variation at a concentration of 10 ng/ml was high because of the dissimilarity of the peak areas of the sample and internal standard. The accuracy of measurement in this instance was considered to be satisfactory for quantitative analysis in a concentration range 5 μ g/ml–50 ng/ml.

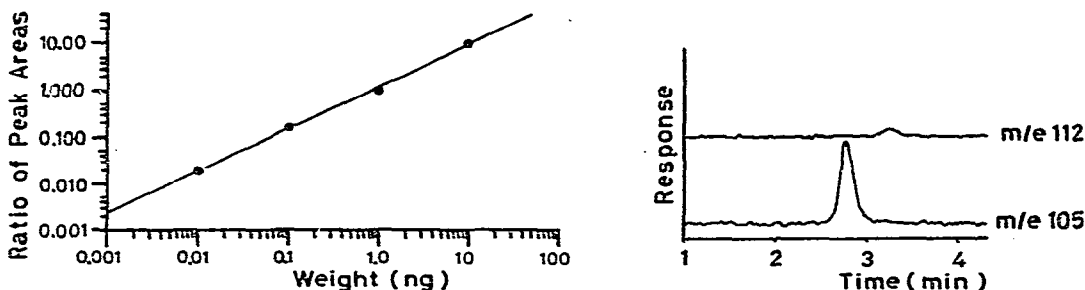


Fig. 1. Calibration graph for geosmin.

Fig. 2. Mass fragmentograms of geosmin (*m/e* 112, 50 pg) and *n*-butyl benzoate (internal standard) (*m/e* 105, 1 ng).

TABLE I
PRECISION OF MEASUREMENT OF GEOSMIN BY GAS CHROMATOGRAPHY-MASS
FRAGMENTOGRAPHY

Concentration present ($\mu\text{g/ml}$)	Concentration found ($\mu\text{g/ml}$)						Coefficient of variation (%)
10	8.68	9.81	8.93	9.70	9.52	9.33	5.4
5	4.74	4.81	5.06	5.00	4.92	4.91	2.4
1.0	1.05	1.05	1.10	1.10	1.08	1.07	1.9
0.5	0.55	0.54	0.51	0.57	0.55	0.54	3.5
0.1	0.11	0.11	0.10	0.10	0.11	0.11	6.4
0.05	0.05	0.04	0.05	0.06	0.04	0.05	18.0

Extended measurement by mass fragmentography with a magnet-type mass spectrometer has been considered to be difficult because the magnetic field is not so stable at a resolution (10% valley) near 1000. In order to study the correction effect for the deviation of the magnetic field by computer, periodic measurements were performed during 4 h, using the standard sample at a concentration of 0.5 $\mu\text{g/ml}$. The results are shown in Table II. The degree of deviation is the same as the measurement accuracy.

TABLE II
PERIODIC MEASUREMENTS OF GEOSMIN (0.5 $\mu\text{g/ml}$) BY GAS CHROMATOGRAPHY-
MASS FRAGMENTOGRAPHY

Time (h)	Concentration found ($\mu\text{g/ml}$)	
	Run 1	Run 2
0	0.55	0.48
1	0.53	0.50
2	0.50	0.45
3	0.50	0.49
4	0.50	0.49

The recovery of geosmin from standard aqueous solution was measured. The results are shown in Table III, the average recovery being 69%. Concentrations of geosmin above 30 ng/l can be measured by this procedure.

TABLE III
RECOVERY OF GEOSMIN FROM STANDARD AQUEOUS SOLUTION BY SOLVENT
EXTRACTION

Amount added ($\mu\text{g/l}$)	Run No.	Recovery (%)	Average recovery (%)
5.0	1	69	69
	2	69	
0.50	1	68	69
	2	70	

As an example of an application, geosmin in the water of the Hanamuro River near Tsukuba New Town was analysed. Sampling was carried out on September 25th, 1978, using two 1-l glass bottles. A musty odour could hardly be detected. The measured geosmin levels results were 31 and 34 ng/l, which are near to the detection limit.

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