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GAS CHROMATOGRAPHIC DETERMINATION OF TRACE AMOUNTS OF β -METHYLMERCAPTOPROPIONALDEHYDE (METHIONAL) IN THE FREE FORM USING FLAME PHOTOMETRIC DETECTION

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SUMMARY

The gas chromatographic (GC) determination of trace amounts of β -methylmercaptpropionaldehyde (methional) in the free form using a flame photometric detector (FPD) was investigated. The GC conditions were as follows: stationary phase, 6% DEGS; support, Chromosorb W HP (80-100 mesh); glass column, 2 m \times 3 mm I.D., column temperature (programming), holding for 1 min at 100°C, heating the column oven at a rate of 10°C/min from 100 to 190°C, maintaining this temperature for 20 min and then cooling to the initial temperature; carrier gas, nitrogen, flow-rate, 60 ml/min; flow-rates of hydrogen and air for the FPD, each 40 ml/min. The minimum detectable amounts for the methional were *ca.* 0.3 ng; the repeatabilities of retention times and peak areas (measured as integrator counts) at 1-ng level of the compound were less than *ca.* 1.5% and *ca.* 15%. The percentage recovery in the concentration method by bubbling the nitrogen carrier gas (0.2 l/min, at 28°C) through the standard solution of methional (at 1 ng per μ l ethanol) from 10 to 0.5 ml was *ca.* 72%; however, the percentage recovery of the standard solution (at 10 ng/ μ l ethanol) after 10 l of the laboratory air had been passed through the impinger containing the standard solution at a rate of 0.5 l/min was 97.5%.

The method was applied to the determination of methional in air over waste water from a corn starch factory.

INTRODUCTION

It is well known that β -methylmercaptpropionaldehyde (methional) is very important as an intermediate in the synthesis of methionine and as a product during the thermal degradation of methionine. Patton¹ has reported that the compound has a broth-like flavour, which is responsible for sunlight flavour defect of milk, and that the flavour and aroma of cooked meats, soup and boiled vegetables frequently suggest the presence of the compound. He also reported that the odour of methional is detectable in milk at a level of 0.05 ppm. However, by sniffing the odour of methional in air using a 14 l Tedlar bag containing a known concentration of the compound, a concentration of 0.7 ppb* was recognisable by trained odour panellists². The com-

* Throughout this article, the American billion (10^9) is meant.

pound is thus very important as specific odourant, being a sulphur-containing lower aliphatic carbonyl compound responsible for the sulphur-like pollution odour in the food industries, because the threshold recognition value of methional in air corresponds to that of methanethiol and diethyl trisulphide^{3,4}.

The determination of methional has been performed by paper chromatography as its 2,4-dinitrophenylhydrazone¹ and by gas chromatography (GC)-mass spectrometry as its *n*-butyl ester⁵. However, there are few reports on the direct determination of methional in its free form.

In this paper, the direct determination of methional in its free form by GC with a flame photometric detector (FPD) is described. The methional-in-air sample was collected in ethanol, through which was bubbled nitrogen carrier gas. The concentrated sample solution was subsequently introduced into the gas chromatograph with an FPD and 6% diethylene glycol succinate polyester (DEGS) on Chromosorb W HP (80-100 mesh) as the column packing. The GC conditions produced peaks with no tailing.

EXPERIMENTAL

Reagents

Acrolein (90-95% purity) was obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Methanethiol (99% purity) was obtained from Seitetsu Kagaku Kogyo (Osaka, Japan). Copper(II) acetate was obtained from Katayama (Osaka, Japan). Ethanol was obtained from Wako (Osaka, Japan). All reagents were of guaranteed or analytical-reagent grade. The column packings were purchased from Wako.

Preparation of methional

Methional was prepared by the method of Pierson⁶. The reaction was carried out by the addition of methanethiol to acrolein, and was catalysed by the addition of a small amount of copper(II) acetate to the reaction mixture, *i.e.*, gaseous methanethiol was bubbled for 30 min with a constant flow of *ca.* 0.7 l/min into a cooled stirred mixture of 56 g of acrolein and 0.5 g of copper(II) acetate, while the temperature of the reaction mixture was maintained at 35-40°C with an ice-water bath. The mixture obtained was stirred for 1 h and then distilled under reduced pressure [b.p. 76-78°C at 34 mmHg, (lit.¹, 71-73°C at 23 mmHg; lit.⁶, 52-57°C at 11 mmHg)], yield 80%.

Standard solutions of the methional were prepared by dissolving the synthesized methional in ethanol to give concentrations of 0.01, 0.1, 1 and 10 mg per 10 ml of ethanol. A calibration graph was obtained using these standard solutions. The volume of the standard solution or the diluted solutions injected into the gas chromatograph was usually 1-5 μ l. A 10- μ l Hamilton 701-N microsyringe was used.

Apparatus

The gas chromatograph used was a Shimadzu Model GC5AP₅Fp (on-column and on-detector system) equipped with an FPD; the FPD had a flame-ionization detector (FID) for monitoring. The FPD and its FID accessory were operated with a separate electrometer (Shimadzu Model EM-5S). The chromatograph was also equipped with a digital integrator (Shimadzu Model ITG-2A) for the determination

TABLE I

EVALUATION OF COLUMN PACKINGS FOR THE DETERMINATION OF TRACE AMOUNTS OF METHIONAL IN THE FREE FORM (FPD DETECTOR, 10 ng)

Carrier gas, nitrogen; flow-rate, 60 ml/min.

<i>Column packing and GC conditions</i>	<i>Evaluations</i>
A 5% TCEP on Carbowack B (60–80 mesh). 1.5 m × 3 mm I.D., glass; 130°C	No peak until 40 min
B 5% SE-30 on Chromosorb W AW DMCS (60–80 mesh), 3 m × 3 mm I.D., glass; 100°C, 1 min holding, 10°C/min programming	Peak at 3.27 min with tailing
C 3% OV-17 on Chromosorb W AW DMCS (60–80 mesh), 3 m × 3 mm I.D., glass; 100°C, 1 min holding, 10°C/min programming	Peak at 5.93 min with tailing
D 6% DEGS on Chromosorb W HP (80–100 mesh), 2 m × 3 mm I.D., glass; 100°C 1 min holding, 10°C/min programming	Peak at 5.40 min without tailing

of retention time and for quantitative analysis. The detector signals were simultaneously recorded at 10 mV b.s.d. on a Shimadzu Model R-201 double-pen recorder.

Operating conditions for gas chromatography

The glass analytical column (2 m × 3 mm I.D.) was packed with 6% DEGS on Chromosorb W HP (80–100 mesh) (Wako). The chromatographic conditions for the FPD were as follows: column temperature (programming), holding for 1 min at 100°C, heating column oven at a rate of 10°C/min from 100 to 190°C, maintaining at this temperature for 20 min and then cooling to the starting temperature; injection port and detector temperature, 200°C; carrier gas (nitrogen) flow-rate, 60 ml/min; flow-rates of hydrogen and air for the FPD, each 40 ml/min. The column was pre-conditioned with the column oven temperature at 200°C for 6 h with a constant flow of nitrogen carrier gas (60 ml/min) before being connected to the FPD.

Collection method for the methional-in-air sample and concentration procedure for the ethanol solution of trace amounts of methional

The collection method for the methional-in-air sample was carried out by using a mini-impinger containing 20 ml of ethanol. The sample gas (10 l) was directly collected in the impinger at 30°C using a Handy Sampler (Model HS-6, Kimoto Electric Industries, Osaka, Japan; maximum sampling rate, 2.5 l/min). The sampling rate was *ca.* 0.5 l/min. The concentration procedure for the ethanol solution containing trace amounts of methional was performed by the nitrogen-gas-bubbling method (0.2 l/min at 28°C).

RESULTS AND DISCUSSION

Evaluation of column packings

Five kinds of column packing were investigated for the GC determination of trace amounts (*ca.* 10 ng) of methional in its free form. As listed in Table I, on the

TABLE II

RELATIVE RETENTION TIMES OF SEVEN SULPHUR-CONTAINING COMPOUNDS ON THE DEGS COLUMN

Retention time of methional = 1.00. Operating conditions for the DEGS column are the same as for condition D in Table I.

<i>Sulphur compound</i>	<i>Relative retention time</i>
Dimethyl disulphide	0.21
Diethyl disulphide	0.32
<i>n</i> -Heptanethiol	0.31
Di- <i>n</i> -butyl disulphide	0.89
Methional	1.00 (true value, 5.40)
Di- <i>n</i> -amyl disulphide	1.37
Diphenyl disulphide	3.00

stationary phases SE-30 (condition B) and OV-17 (condition C) on Chromosorb W AW DMCS (60–80 mesh), the methional peak tailed.

In the TCEP on Carboxpack B^{7,8} stationary phase, which was used for the determination of the lower aliphatic carbonyl compounds in their free forms, the peak was not detected until 40 min. Under these conditions, the retention time of *n*-valeraldehyde (C₅) was *ca.* 2.5 min. Use of DEGS on Chromosorb W HP as stationary phase, however, gave a well resolved peak for methional with no tailing.

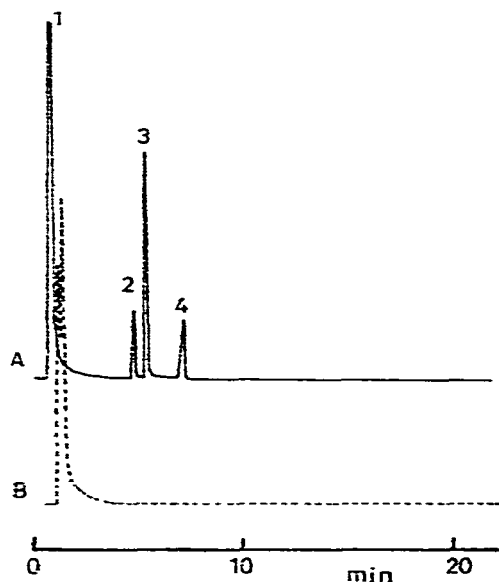


Fig. 1. Typical gas chromatograms of methional, di-*n*-butyl disulphide and di-*n*-amyl disulphide. Chromatogram A: FPD sensitivity, 16×10 . Peaks: 1 = ethanol; 2 = di-*n*-butyl disulphide (1 ng); 3 = methional (2 ng); 4 = di-*n*-amyl disulphide. Chromatogram B: FID (monitor), sensitivity, 16×10 . 6% DEGS on Chromosorb W-HP (80–100 mesh), 2 m \times 3 mm I.D., glass; temperature programming, holding for 1 min at 100°C, heating the column oven at 10°C per min from 100 to 190°C, maintaining at this temperature for 20 min and then cooling to the starting temperature; nitrogen carrier gas, flow-rate 60 ml/min.

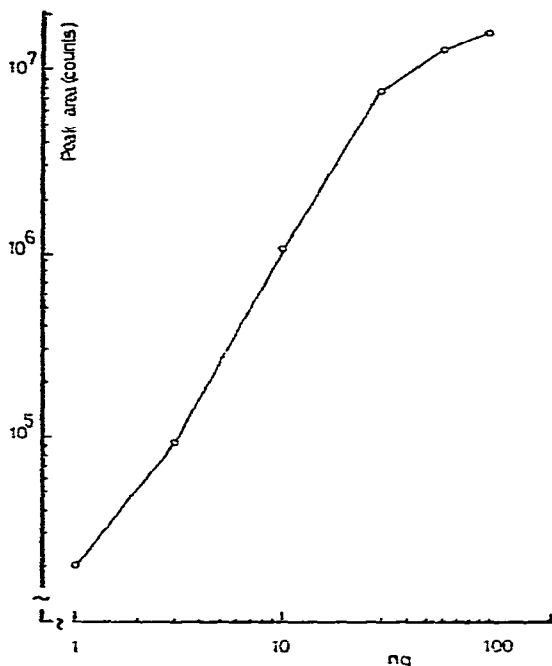


Fig. 2. Calibration graph for methional in its free form with FPD.

The retention times of seven sulphur containing compounds under the GC conditions labelled as D in Table I, are listed in Table II. The amount of each sulphur-containing compound used was 5 ng.

Fig. 1 shows a typical gas chromatogram of methional, di-*n*-butyl disulphide and di-*n*-amyl disulphide. The peak of the methional in its free form occurred between the peaks of di-*n*-butyl disulphide and di-*n*-amyl disulphide with no tailing. Fig. 1 shows that under the GC conditions D of Table I, these conditions are the test for a rapid, specific and sensitive detection of methional in its free form.

Calibration graph

The FPD response produced a straight line in the approximate range 1–30 ng of methional in its free form (Fig. 2), and the detection limit (at twice the noise level) was *ca.* 0.3 ng.

Repeatability of retention times and peak areas for methional in its free form

The repeatability and uniformity of the retention times and the peak area (as counts of the digital integrator) for the methional in its free form were evaluated by using 1- and 10-ng amounts. Table III shows that there was good repeatability.

Percentage recovery in the concentration procedure of the methional-ethanol standard solution

Table IV lists the percentage recovery in the concentration procedure of the standard solution (1 ng/ μ l) by the bubbling method with a constant flow of nitrogen

TABLE III

REPEATABILITY OF RETENTION TIMES AND PEAK AREAS FOR METHIONAL IN ITS FREE FORM ON THE DEGS COLUMN ($n = 7$)

Operating conditions for the DEGS column are the same as for conditions D in Table I.

	1 ng		10 ng	
	Retention time (min)	Peak area (counts $\times 10^3$)	Retention time (min)	Peak area (counts $\times 10^3$)
Average	5.39	19	5.44	1091
S.D.	0.02	3	0.08	82
Coefficient of variation (%)	0.4	15.8	1.5	7.5

carrier gas (0.2 l/min) at 28°C for 6 h, and after 10 l of laboratory air had passed through the standard solution (10 ng/ μ l). These tests were required for preliminary information on the oxidative degradation and photolysis of methional. Table IV shows that no interference by the presence of air was observed; however, loss of methional during the bubbling procedure occurred.

Typical gas chromatogram of methional-in-air sample collected from over waste water from a corn starch factory

Fig. 3 shows a typical gas chromatogram for a sample of methional and other sulphur-containing compounds in air collected from over waste water from a corn starch factory. The procedure for preparation of concentrated solution was as described in the Experimental section. The volume of the concentrated sample solution injected was 50 μ l. The FPD, which is selective for analysis of sulphur compounds, permits the use of large sample volumes. Thus the merit of this method is that up to 50 μ l of the sample solution can be used. The concentration of the methional in free form in the air sample was *ca.* 0.5 ppb. The odour characteristics (quality and intensity) of the air sample were sulphur-like and moderate.

CONCLUSION

The direct gas-chromatographic determination of the trace concentration of a methional-in-air sample, using a DEGS on Chromosorb W HP column with detec-

TABLE IV

PERCENTAGE RECOVERIES OF THE METHIONAL FROM ETHANOL STANDARD SOLUTIONS

Conditions	Recovery (%)
(a) After passage of 10 l of laboratory air through the standard solution (10 ng/ μ l) in 10-ml impinger	97.5
(b) After concentration of the standard solution (1 ng/ μ l) from 10 to 0.5 ml with a nitrogen carrier gas flow of 0.2 l/min at 28°C for 6 h	72.6

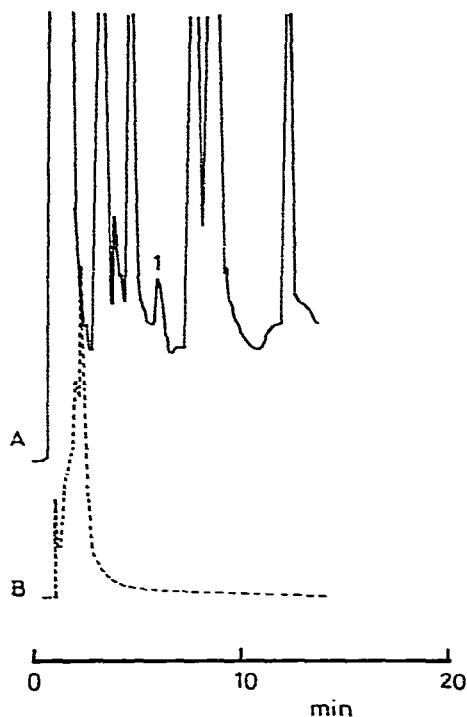


Fig. 3. Typical gas chromatogram of methional in its free form from air sample collected from over waste water from a corn starch factory. Chromatogram A: FPD sensitivity, 16×10 . Peak: 1 = methional (ca. 0.5 ppb). Chromatogram B: FID (monitor), sensitivity, 16×10 . Sample gas, 10 l collected into 20 ml ethanol impinger at 0.5 l/min, then 10 ml of the ethanol solution concentrated to 0.5 ml, 50 μ l injected.

tion by FPD, has been demonstrated. The proposed method may be capable of giving rapid, sensitive and specific detection of both methional in its free form in air and of odour pollution related to food industries, etc.

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