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GAS CHROMATOGRAPHIC DETERMINATION OF SULPHUR COMPOUNDS IN TOWN GAS

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SUMMARY

The gas chromatographic (GC) determination of the sulphur compounds in town gas (in the Nagoya area) was studied by using a flame-photometric detector (FPD) and the cold-trap method with liquid oxygen. The column packings used were 25% TCEP on Shimalite (AW, DMCS), 25% TCP on Shimalite (AW, DMCS), 10% PPE on Shimalite TPA, Porapak Q and silica gel.

The major components identified were carbonyl sulphide, hydrogen sulphide, carbon disulphide, thiophene and tetrahydrothiophene (THT). The identities of thiophene and THT were also confirmed by GC combined with the use of a quadrupole mass spectrometer.

The average concentrations and standard deviations of thiophene and THT were 8.8 ± 1.8 and 124 ± 35 ng per 0.05 l, respectively. The latter value corresponds to 0.7 ppm, which is relatively high for the concentration of an odorant.

INTRODUCTION

In Japan, coal gas has been widely used as town gas and it is therefore important that the gas should possess a distinctive smell, so that accidental carbon monoxide poisoning can be avoided as far as possible. In the U.S.A. three types of odorant have been used: mercaptans, aliphatic sulphides and cyclic sulphides, such as tetrahydrothiophene (THT)¹, which is chemically stable, economical and easy to add to gas. In Japan, the use of THT has also been reported², but information on the constituents of the sulphur compounds in town gas is sparse.

The analysis of sulphur compounds by using a flame-photometric detector (FPD)³⁻²⁴ is common because of its relative specificity to the sulphur-containing molecules, its sensitivity and the possibility of combining it with gas chromatography (GC). The FPD response to sulphur compounds is based on the formation of activated S_2^* molecules and their subsequent chemiluminescent emission in hydrogen-rich flames.

This paper describes the GC determination of the sulphur compounds in town gas in the Nagoya area by using the FPD-GC technique and the cold-trap method with liquid oxygen²⁵⁻²⁷. The main peaks in the gas chromatogram using an FPD, *i.e.*, thiophene and THT, were also identified by GC combined with the use of a quadrupole mass spectrometer (GC-QMS).

EXPERIMENTAL

Apparatus

The gas chromatograph used was a Shimadzu Model GC5AP₅FFp equipped with an FPD and a digital integrator (Shimadzu Model ITG-2A) for calibration and quantitative analysis. The operating conditions and column packings are given in Table I.

TABLE I
OPERATING CONDITIONS FOR GC ANALYSIS

Condition	a	b	c	d	e
Column packing	25% TCEP on Shimalite (AW, DMCS), 60-80 mesh	25% TCP on Shimalite (AW, DMCS), 60-80 mesh	10% PPE on Shimalite TPA, 60-80 mesh	Porapak Q, 50-80 mesh	Silica gel, 60-80 mesh
Main column (glass)	3 m × 3 mm I.D.	3 m × 3 mm I.D.	3 m × 3 mm I.D.	3 m × 3 mm I.D.	3 m × 3 mm I.D.
Pre-column (glass)	31 cm × 4 mm I.D.	31 cm × 4 mm I.D.	31 cm × 4 mm I.D.	31 cm × 4 mm I.D.	31 cm × 4 mm I.D.
Temperature (°C):					
Column	70	70	40	140	130
Injection	150	150	150	200	250
Detector	205	210	205	210	210
Flow-rate (ml/min):					
N ₂ (carrier gas)	50	50	50	50	50
H ₂	40	40	40	40	40
Air	40	40	40	40	40

The same packing was used in the main column and pre-column. The operating conditions and settings for the digital integrator were as follows: baseline corrector threshold, $\infty \mu\text{V}$; delay, 5 sec; filter digital, 1000; noise, M; peak detector, $50 \mu\text{V}/\text{min}$.

The apparatus used for GC-QMS was a Finnigan Model 3300E instrument. The operating conditions were as follows. For GC: stationary phase, 25% TCEP; column, 1.5 m × 1.7 mm I.D.; column temperature, 100°; injection temperature, 150°; separator temperature, 230°; carrier gas, helium (3.0 kg/cm²). For QMS: sensitivity, 10^{-7} A/V ; filter, 0.5 U/sec; first MS, 0; last MS, 100; applied voltage to electron multiplier, 1800 V; electron energy, 63 V; collector current, 0.48 mA; programmable multiple ion monitor MS for mass fragmentography, 60, 84, 88; time, 10 msec; filter, 0.5 Hz.

Reagents

THT was obtained from Wako (Osaka, Japan); all other reagents used have been described earlier^{25,27}.

Analytical procedure

FPD-GC analysis. The sample gas (0.05–0.1 l) was collected in the pre-column by using a cold trap with liquid oxygen, then the pre-column was connected to the carrier-gas line with cooling with liquid oxygen. After about 15 min (necessary for the elution of bulky lower hydrocarbons), the pre-column was heated from -183° to $+100^{\circ}$ for injection of the condensed sample into the gas chromatograph.

GC-QMS analysis. The sample gas (30 l) was collected by using a cold trap with liquid oxygen and *n*-hexane (8 ml) was added to the condensate.

RESULTS AND DISCUSSION

Typical gas chromatogram by the FPD-GC

Fig. 1 shows a typical gas chromatogram of the sulphur compounds in the town gas obtained using a TCEP column packing. At least twelve representative sulphur compounds, such as carbonyl sulphide, hydrogen sulphide, carbon disulphide, thiophene and THT, were identified from the relative retention time table²⁷.

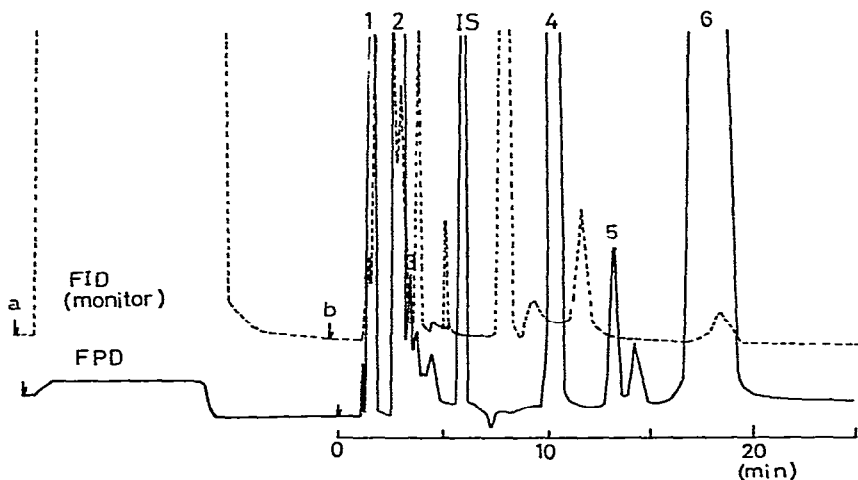


Fig. 1. Typical gas chromatogram of the sulphur compounds in the town gas obtained with a TCEP column under GC conditions (a) in Table I. Sample volume, 0.1 l. Peaks of sulphur compounds: 1 = carbonyl sulphide and hydrogen sulphide; 2 = carbon disulphide and methyl mercaptan; 3 = ethyl, isopropyl and *tert.*-butyl mercaptan; 4 = thiophene; 5 = dimethyl disulphide and *n*-hexyl mercaptan, 6 = THT and allyl sulphide; IS (internal standard) = diethyl sulphide (gas), 8 ng. Position a represents the carrier line and position b represents the pre-column heating.

Peaks 1, 2 and 3 were obtained as a result of the “quenching” effect due to hydrocarbons of large molecular volume and the identification of these sulphur compounds was difficult. However, the peaks of thiophene and THT did not suffer from interference from other organic compounds. The peak of THT overlapped with

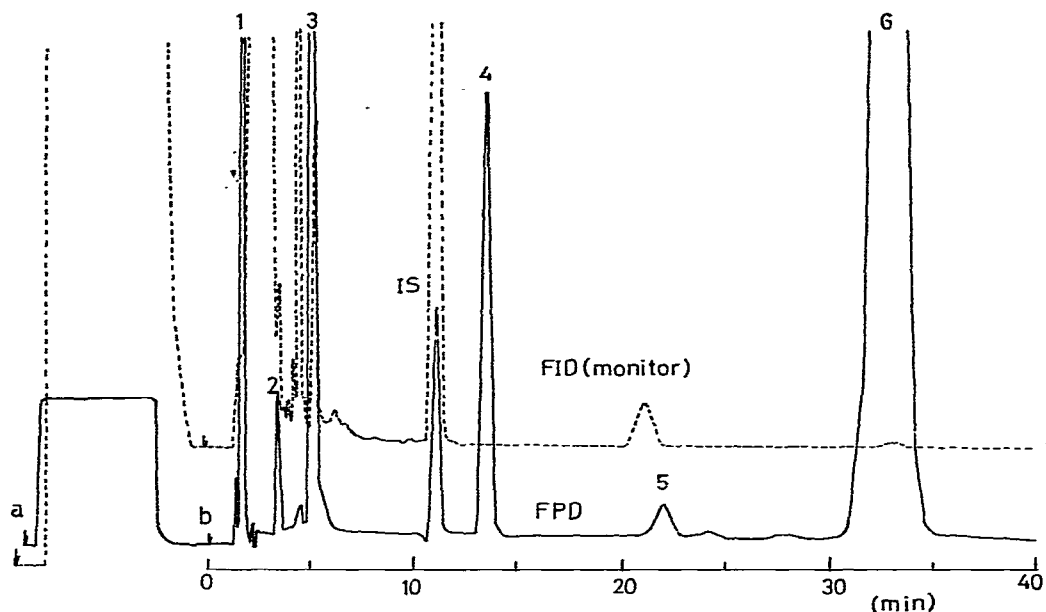


Fig. 2. Typical gas chromatogram of the sulphur compounds in the town gas obtained with a TCP column under GC conditions (b) in Table I. Sample volume, 0.05 l. Peaks of sulphur compounds: 1 = carbonyl sulphide and hydrogen sulphide; 2 = sulphur dioxide; 3 = dimethyl sulphide, carbon disulphide and isopropyl mercaptan; 4 = thiophene; 5 = dimethyl disulphide and *n*-butyl methyl sulphide; 6 = THT and *tert*-butyl sulphide; IS (internal standard) = diethyl sulphide (gas), 4 ng. Positions a and b as in Fig. 1.

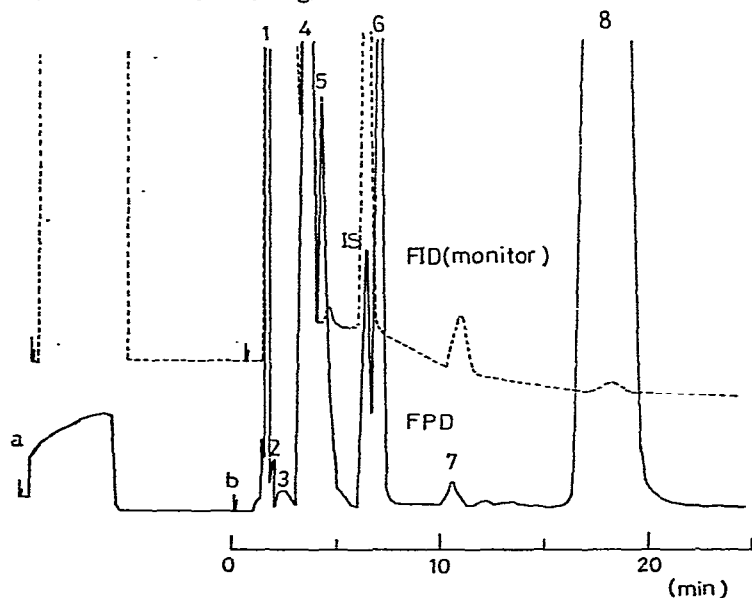


Fig. 3. Typical gas chromatogram of the sulphur compounds in the town gas obtained with a PPE column under GC conditions (c) in Table I. Sample volume, 0.05 l. Peaks of sulphur compounds: 1 = carbonyl sulphide, hydrogen sulphide and sulphur dioxide; 2 = methyl mercaptan; 3 = ethyl mercaptan and dimethyl sulphide; 4 = *n*-propyl mercaptan and carbon disulphide; 5 = ethyl methyl sulphide; 6 = *n*-butyl mercaptan and thiophene; 7 = dimethyl disulphide; 8 = THT; IS (internal standard) = diethyl sulphide (gas), 4 ng. Positions a and b as in Fig. 1.

that of allyl sulphide but, as shown in Fig. 1, the main peak of the sulphur compounds in the town gas was due to THT.

Fig. 2 shows a typical gas chromatogram of the sulphur compounds in the town gas obtained using a TCP column packing. At least eleven sulphur compounds, such as carbonyl sulphide, hydrogen sulphide, carbon disulphide, thiophene and THT, were identified. The peaks of thiophene and THT did not suffer from interference from the other organic compounds, but the peak of THT overlapped with that of *tert.*-butyl sulphide.

Fig. 3 shows a typical gas chromatogram of the sulphur compounds in the town gas obtained using a PPE column packing. The peak of THT did not suffer from interference from the other sulphur compounds.

For the identification of THT, PPE was the best column packing.

Fig. 4 shows a typical gas chromatogram of the sulphur compounds in the town gas obtained using a Porapak Q column packing. Hydrogen sulphide was eluted more rapidly than carbonyl sulphide, and this column is therefore superior for the identification of the former, although a long elution time for the complete elution of thiophene and THT is necessary.

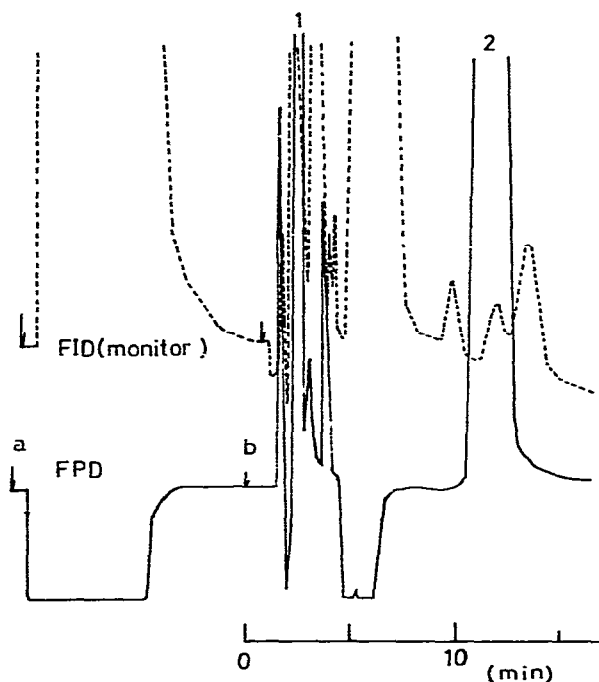


Fig. 4. Typical gas chromatogram of the sulphur compounds in the town gas obtained with a Porapak Q column under GC conditions (d) in Table I. Sample volume, 0.05 l. Peaks of sulphur compounds: 1 = hydrogen sulphide and carbonyl sulphide; 2 = carbon disulphide. Positions a and b as in Fig. 1.

Fig. 5 shows a typical gas chromatogram of the sulphur compounds in the town gas obtained using a silica gel column packing. This column is superior for the identification of carbonyl sulphide, but a long elution time for the complete elution

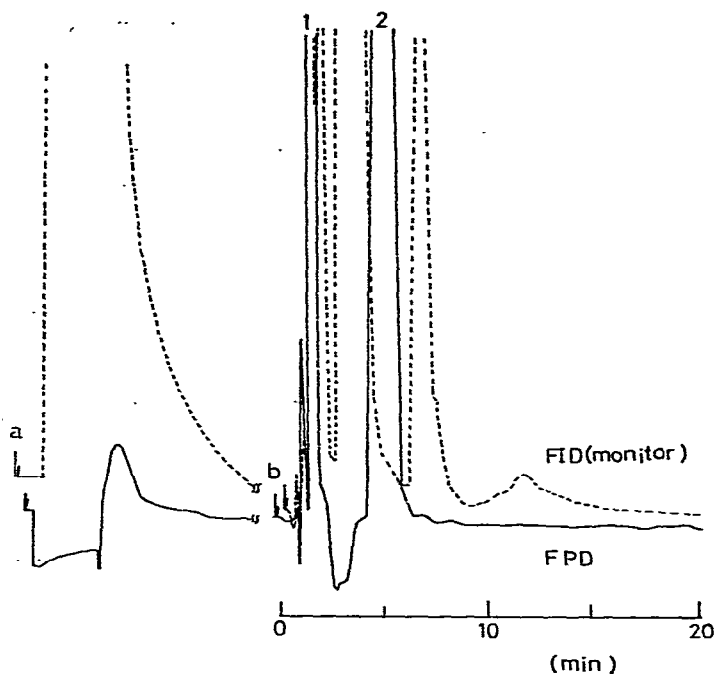


Fig. 5. Typical gas chromatogram of the sulphur compounds in the town gas obtained with a silica gel column under GC conditions (e) in Table I. Sample volume, 0.05 l. Peaks of sulphur compounds: 1 = carbonyl sulphide; 2 = carbon disulphide. Positions a and b as in Fig. 1.

of thiophene and THT is necessary. Hydrogen sulphide was not identified because of the "Quenching" effect of hydrocarbons of large molecular volume.

Mass spectrometry

Fig. 6 shows a chromatogram obtained by total ion monitoring (TIM) of 2 μ l of sample solution prepared as described under *GC-QMS analysis*. Peaks 1 and 2 corresponded with the elution positions of thiophene and THT, respectively.

Fig. 7a and 7b shows the mass spectra of peaks 1 and 2, respectively, in the TIM chromatogram (Fig. 6). As shown in Fig. 7a, the base peak is at m/e 91, which corresponds to toluene, and the peak at m/e 84 corresponds to the parent ion of thiophene, but the latter peak is small. Therefore, the identification of thiophene from the mass spectrum was not confirmed.

However, in Fig. 7b the base peak is at m/e 60, and next in abundance is the peak at m/e 88, which indicated the presence of THT. The abundance of the m/e 88 peak relative to the base peak is about 50%. Therefore, the identification of THT from the mass spectrum was confirmed.

Fig. 8a and 8b shows the mass fragmentograms (m/e at 60, 84 and 88, triple channel) of 1 μ l of the sample solution and of 10 ng of the authentic compounds, respectively. The m/e 84 and 88 peaks are parent peaks of thiophene and THT, and the m/e 60 peak is the base peak or the peak of secondary abundance in each mass spectrum.

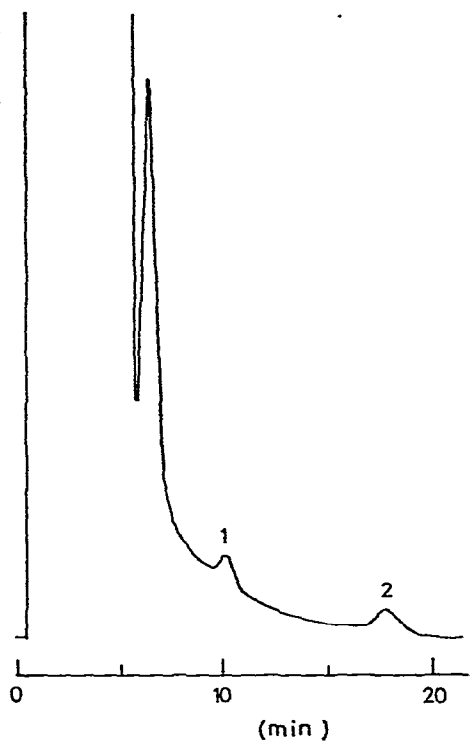


Fig. 6. Chromatogram obtained by TIM of $2\mu\text{l}$ of sample solution prepared as described under GC-QMS analysis. Peaks 1 and 2 corresponded with the elution positions of thiophene and THT, respectively.

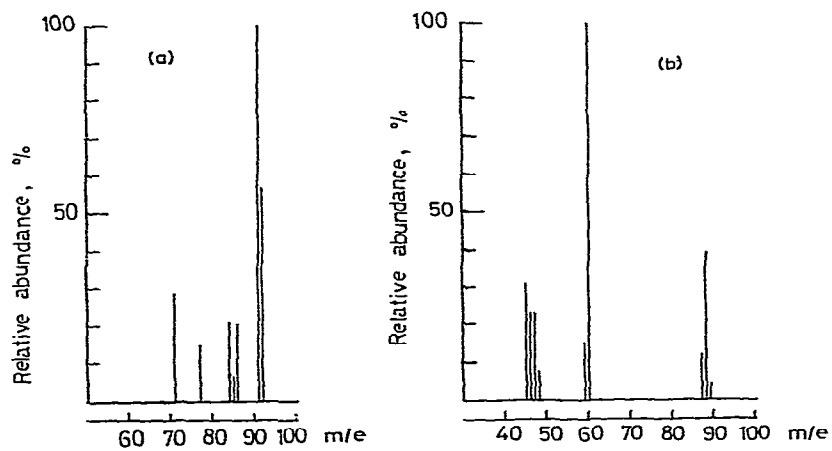


Fig. 7. Mass spectra of the peaks in the chromatograms in Fig. 6 obtained by TIM: (a) peak 1; (b) peak 2.

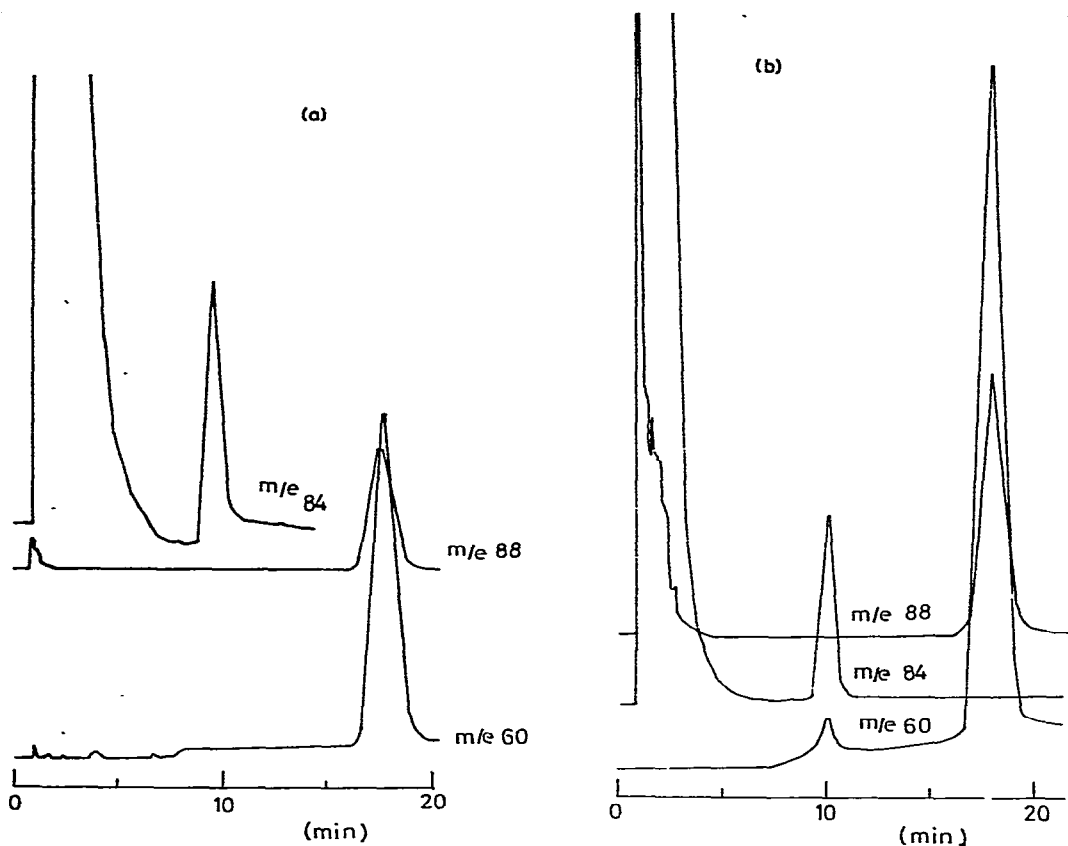


Fig. 8. (a) Mass fragmentograms of 1 μ l of sample solution prepared as described under *GC-QMS analysis*. (b) Mass fragmentograms of 10 ng of thiophene and THT (authentic compounds). The sample volume injected was 1 μ l.

In the mass fragmentograms of the authentic compounds, the peaks at m/e 60 and 84 correspond with the elution positions of thiophene, and that at m/e 60 and 88 correspond with the elution position of THT. Therefore, the identifications of thiophene and THT were confirmed by the mass fragmentograms at m/e 60, 84 and 88.

Calibration graphs of thiophene and THT obtained with the FPD

Fig. 9 shows the calibration graphs for thiophene and THT obtained using a 25% TCEP column packing. The detector response produced linear relationships in the range 4–20 ng for thiophene and 8–100 ng for THT.

Quantitative results

Results for the determination of thiophene and THT in samples of town gas from the Nagoya area are given in Table II. The average concentrations and standard deviations for thiophene and THT were 8.8 ± 1.8 and 124 ± 35 ng per 0.05 l, respectively. This value of THT corresponds to about 0.7 ppm, which is relatively high for the concentration of an odorant.

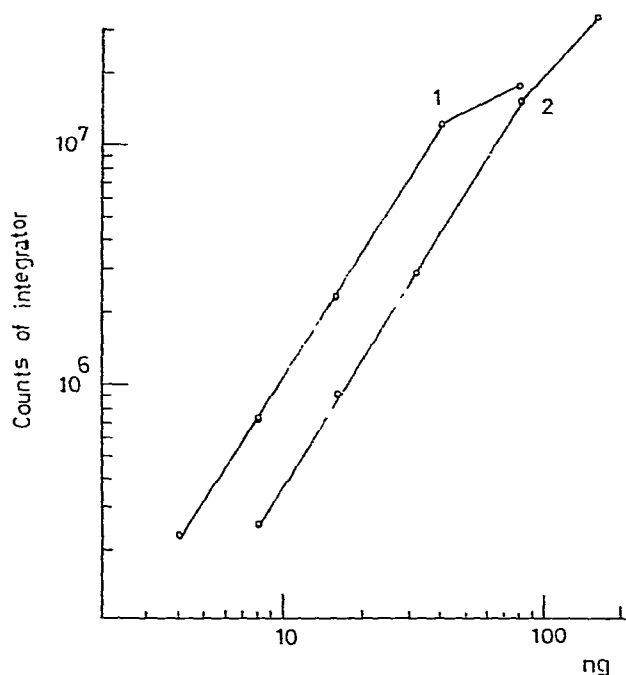


Fig. 9. Calibration graphs for (1) thiophene and (2) THT obtained with the FPD using a TCEP column under GC conditions (a) in Table I.

TABLE II

RESULTS FOR THE DETERMINATION OF THIOPHENE AND THT IN TOWN GAS IN THE NAGOYA AREA

Six samples were taken and analyzed on May 18th, 1976.

Sample No.	Thiophene (ng per 0.05 l)	THT (ng per 0.05 l)
1	9.0	75
2	7.5	140
3	5.5	72
4	9.5	150
5	10.5	150
6	10.5	155
Average	8.8	124
Standard deviation	±1.8	±35

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