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IMPROVED GAS CHROMATOGRAPHIC OZONE CHEMILUMINESCENCE DETECTOR

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SUMMARY

A reactor chamber for an ozone chemiluminescence detector is described, in which the geometry has been modified and the internal volume minimized. Selectivity can be obtained through variations in their reactivity towards ozone of different classes of compounds, and can be adjusted by means of the detector temperature and the ozone flow-rate. The detector gives linear responses for C₆-C₉ hydrocarbons and thiophenes.

INTRODUCTION

Recently, we described¹ a novel selective detector for gas chromatography which utilized the chemiluminescence of ozone reactions as a means of detection. The system proved to be sensitive to mass flow-rate and provided linear responses for different types of hydrocarbons over several orders of magnitude. The sensitivity and the detection limit were temperature dependent and the latter frequently reached the nanogram level.

The detector was applied successfully to the analysis of light hydrocarbons. However, the analysis of heavier hydrocarbons was difficult because of pronounced peak tailing caused by the adsorption of compounds on the surface of the reaction chamber. This adsorption was favoured by temperature gradients.

This paper reports the results obtained with a modified reactor that has improved thermal and flow properties. The reactor design and its influence on the detector characteristics are discussed. Chromatograms with particular emphasis on hydrocarbon selectivity are presented, and the detection of thiophenes is evaluated.

EXPERIMENTAL

Apparatus

The instrumentation was basically the same as that reported previously¹. The

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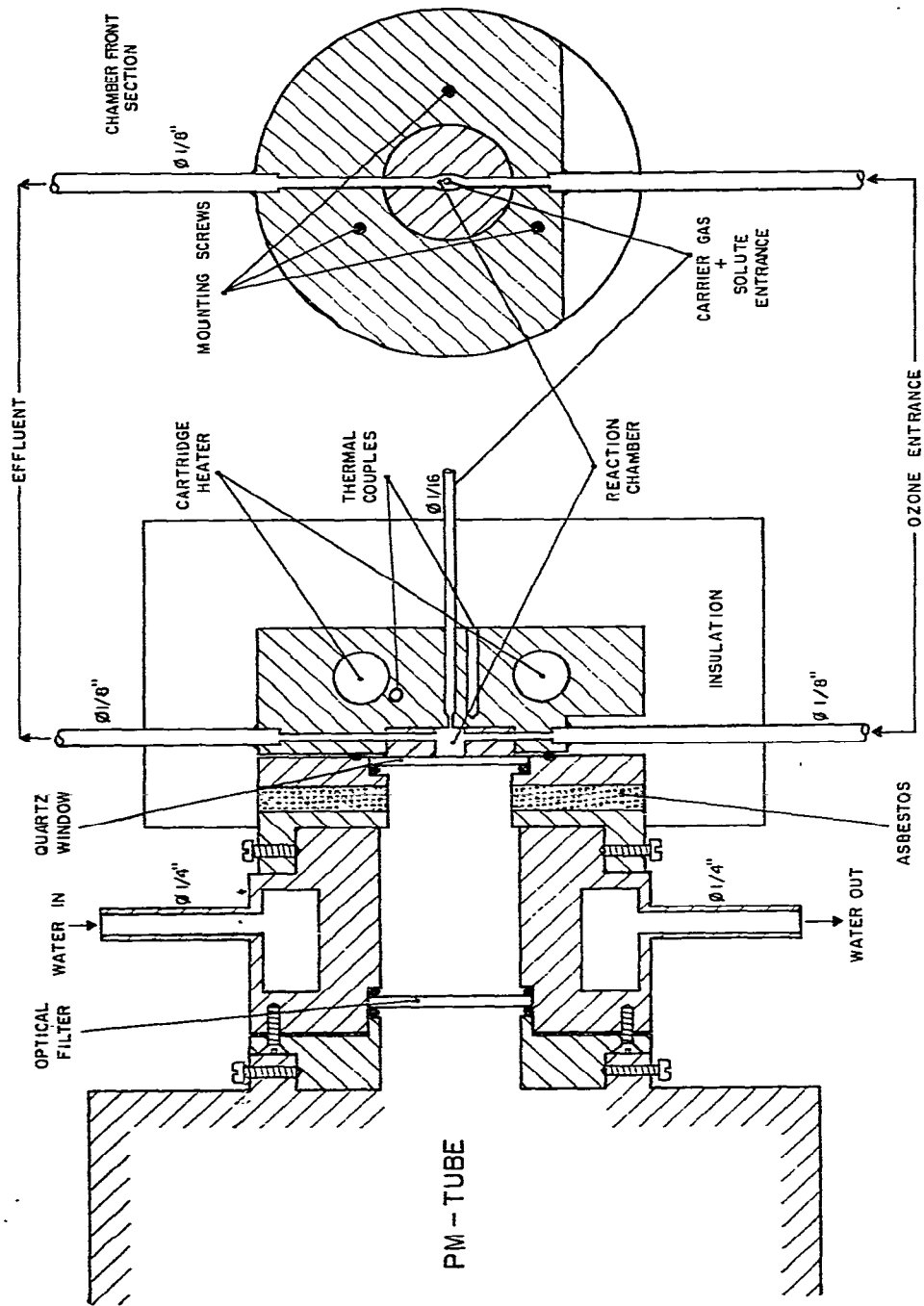


Fig. 1. Schematic diagram of the reactor and heat exchanger.

sampling device and the column oven were replaced with a Model C.G.-17 gas chromatograph (Instrumentos Científicos C.G. Ltda, São Paulo, Brazil) equipped with a hydrogen flame-ionization detector.

The modified reactor is shown in Fig. 1. In contrast to that used previously, the column effluent and the ozone do not enter it in parallel streams but perpendicular to each other. Furthermore, the chamber volume (about 0.6 ml) is considerably less than before (1.8 ml). The chamber is oval-shaped with the ozone entrance and exit at its extremities.

The reactor wall adjacent to the heat exchanger was insulated with an asbestos plate, and the pre-heater was omitted because it proved to be ineffective.

Columns. The hydrocarbon analyses were performed in a $3\text{ m} \times \frac{5}{64}$ in. I.D. stainless-steel column packed with 10% pre-tested diethylene glycol succinate, Hi-EFF 1 BP, on 100–150-mesh Porasil C (both from Applied Science Labs., State College, Pa., U.S.A.). The behaviour of thiophene was investigated on a $25\text{ cm} \times \frac{5}{64}$ in. I.D. column containing Pennwalt 223 G.C. on Gas-Chrom R, 80–100 mesh (Applied Science Labs.).

Standards

The hydrocarbon standards were obtained from Phillips Petroleum (Bartlesville, Okla., U.S.A.) and the thiophenes from Aldrich (Milwaukee, Wisc., U.S.A.).

RESULTS AND DISCUSSION

The main cause of peak tailing and reduced selectivity of the detector is the residence time of the solutes in the reaction chamber. The modified reactor was designed in order to decrease the residence time, and the chamber volume was therefore considerably reduced and the geometries of the chamber and the ozone entrance were modified in order to avoid turbulence. Also, the thermal insulation of the chamber was improved in order to minimize temperature gradients. The maximum operating temperature of the detector was 200° in order to prevent the thermal decomposition of ozone and an increase of the zero background.

The detector selectivity is mainly the result of the different reactivities of ozone towards different classes of compounds. Furthermore, the selectivity can be varied by using different detector operating conditions (temperature, flow-rate). This behaviour can be easily understood on the basis of a chemical ozone reaction, in which the temperature of the detector has a direct influence on the reaction velocity and the flow-rate of the ozone mixture ($\text{O}_3\text{-O}_2$) on the chamber residence time. Therefore, the detector response increases with the chamber temperature and decreases with the flow-rate of the ozone mixture.

The main characteristics of the detector, namely linearity, sensitivity, detectability and specificity, were determined by injecting $5\ \mu\text{l}$ of *n*-pentane solutions of the compounds to be detected. The hydrocarbons were injected into the diethylene glycol succinate column, which provided an efficiency of 1600 theoretical plates for hexene. The thiophenes were evaluated in the Pennwalt column, the efficiency of which for thiophene was 2540 theoretical plates.

The ozone concentration in the $\text{O}_3\text{-O}_2$ mixture was maintained at 80 mg/l in

all of the experiments. However, three different flow-rates were used (300, 200 and 100 ml/min) in order to evaluate its influence on the detector characteristics.

Logarithmic graphs of peak area *versus* amount of sample are shown in Figs. 2-5 in order to demonstrate the linearity of the detector response. All of the hexene curves had a slope of 1.0. The upper limit of the linear range was not determined because the use of more concentrated solutions resulted in overloading of the columns. The detector response for benzene at 150° and 200° was linear only at an ozone mixture flow-rate of 300 ml/min; at lower flow-rates the non-linear response indicated that the chemiluminescent reaction was not a single-step process. The signal from thiophene was linear up to about 5 μg of sample; for larger amounts the graphs had a slope of 2.0, suggesting a second-order reaction for thiophene. The 2-methylthiophene graphs gave a slope of 1.0 up to about 10 μg of sample injected.

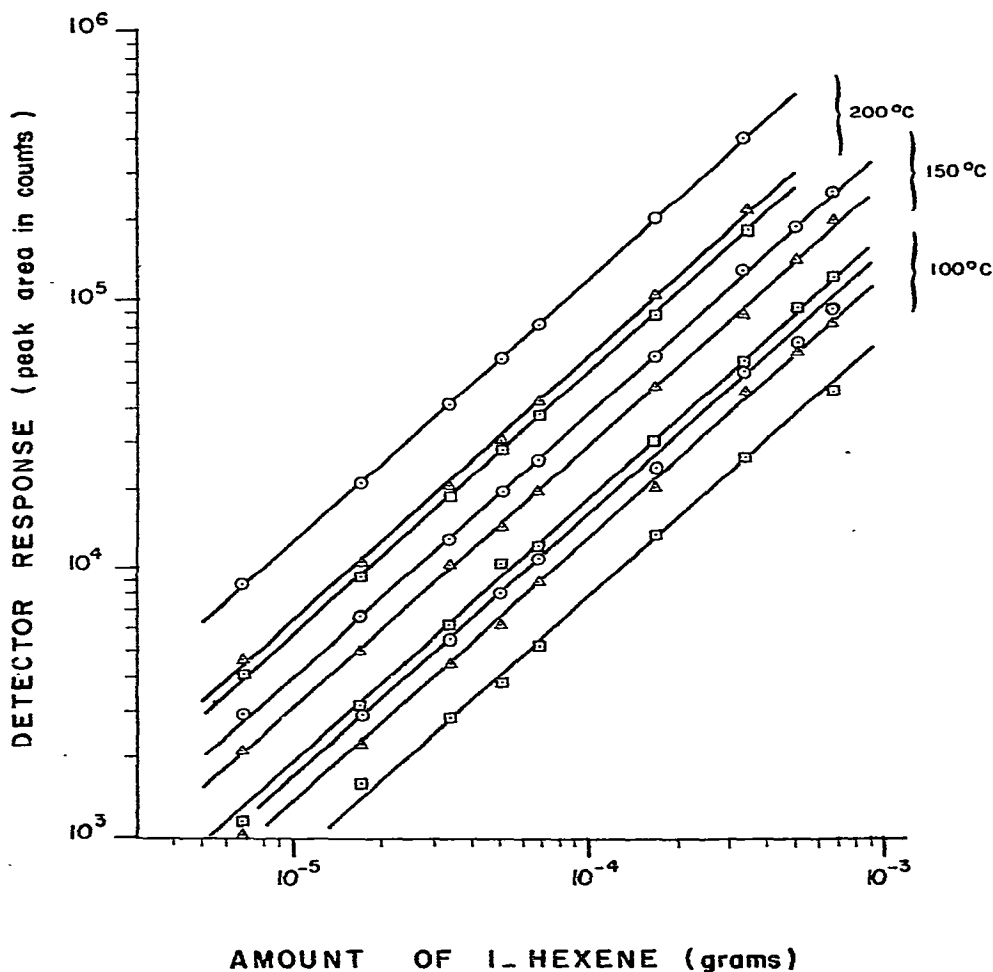


Fig. 2. Detector linearity: area response as a function of amount of 1-hexene and flow-rate of ozone mixture. \circ = 100 ml/min; \triangle = 200 ml/min; \square = 300 ml/min.

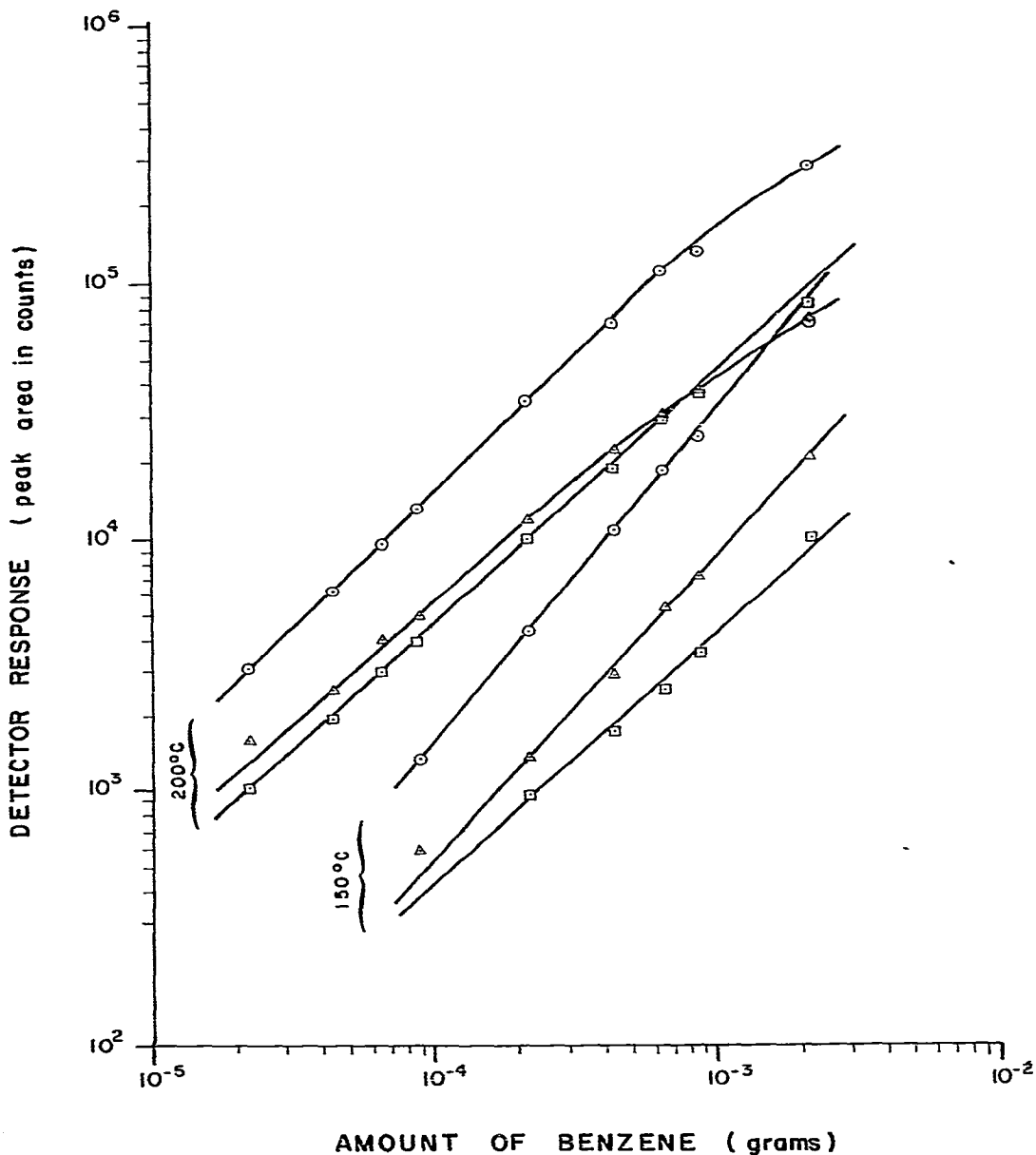


Fig. 3. Detector linearity: area response as a function of amount of benzene and flow-rate of ozone mixture. \odot = 100 ml/min; \triangle = 200 ml/min; \square = 300 ml/min.

Linear ranges were obtained for all of the compounds studied, thus providing a good basis for quantitative analysis. The sensitivity, detectability and specificity are presented in Tables I-IV.

Results for benzene at 100° and for heptane at 100° and 150° were not obtained

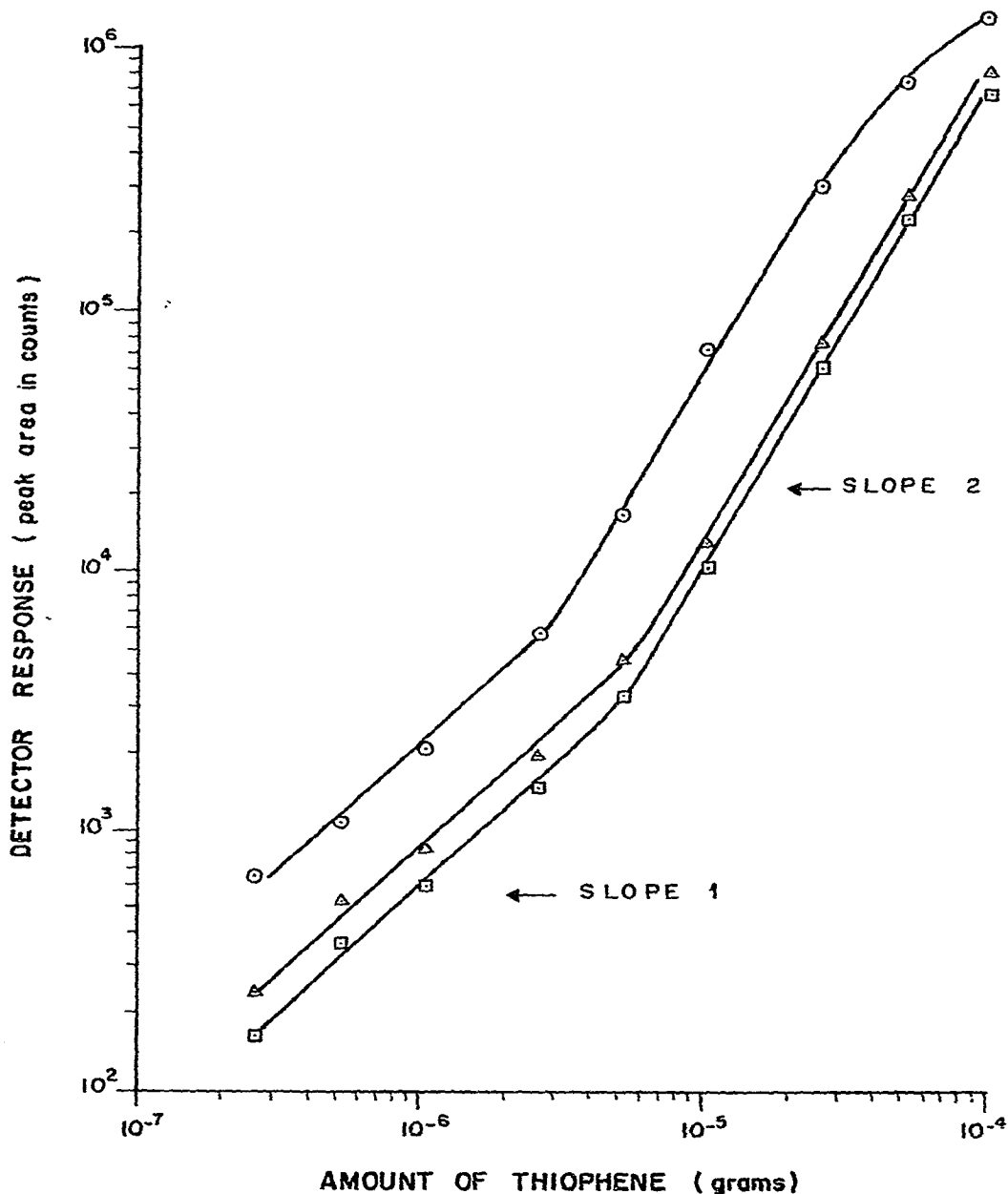


Fig. 4. Detector linearity: area response as a function of amount of thiophene and flow-rate of ozone mixture. ○ = 100 ml/min; △ = 200 ml/min; □ = 300 ml/min.

because larger amounts of sample were necessary, which caused overloading of the columns.

The sensitivity and detectability for all compounds were calculated relative to their linear response ranges. For benzene, the sensitivity and detectability were cal-

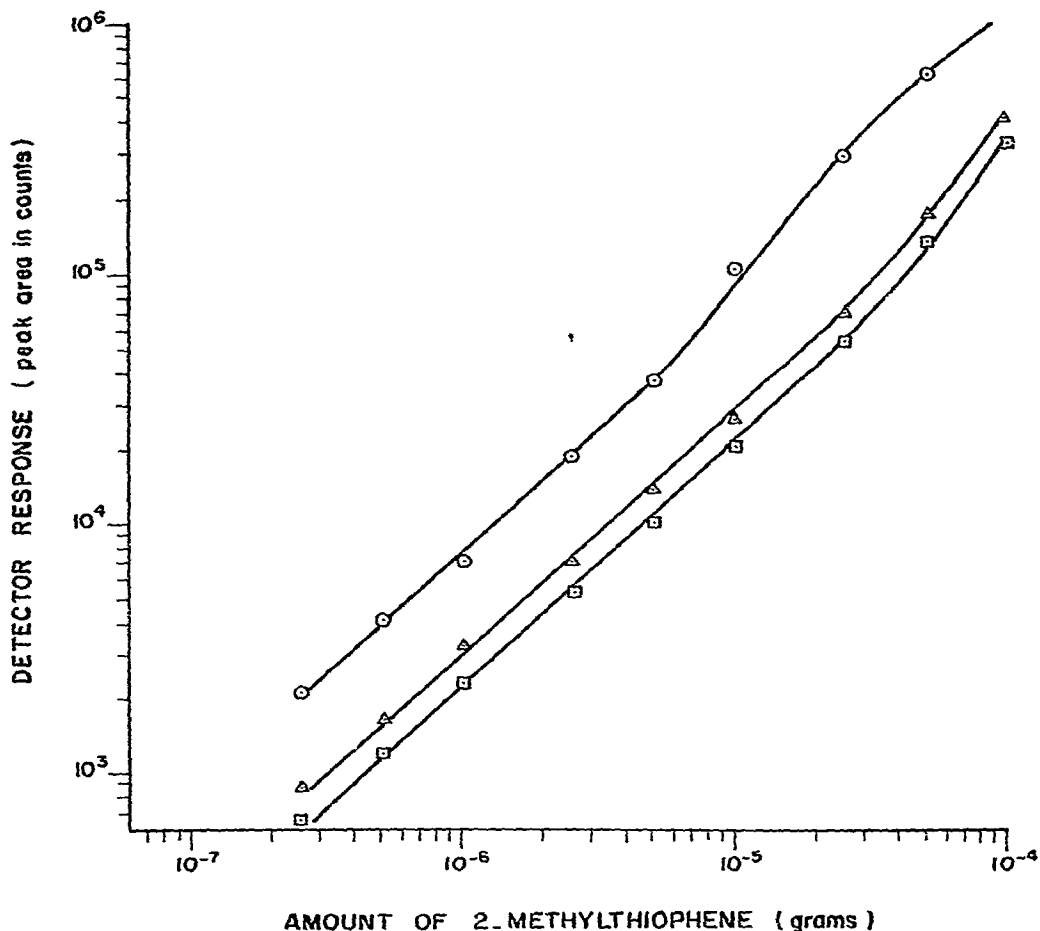


Fig. 5. Detector linearity: area response as a function of amount of 2-methylthiophene and flow-rate of ozone mixture. ○ = 100 ml/min; △ = 200 ml/min; □ = 300 ml/min.

culated relative to $5.63 \cdot 10^{-6}$ mole because this compound gives a linear response only at an ozone mixture flow-rate of 300 ml/min. For thiophene, sensitivity and detectability values (Table IV) were also calculated from its exponential range. The detector sensitivity for thiophene and 2-methylthiophene was one order of magnitude higher than for hexene. Consequently, the selectivity was also very high.

Applications

The ozone chemiluminescence detector was applied to the analysis of a synthetic C_6 - C_9 hydrocarbon mixture containing saturated (normal, cyclic and branched-chain), olefinic and aromatic hydrocarbons. The chromatograms are presented in Fig. 6. Five runs were carried out at ozone chemiluminescence detector temperatures of 100–250°, and one for the hydrogen flame-ionization detector. Peak tailing did not occur even when the reaction chamber was operated at 100°. The

TABLE I

DETECTOR SENSITIVITY FOR DIFFERENT TYPES OF COMPOUNDS

Calculated as peak area/mole (counts/mole).

Temperature (°C)	Ozone flow-rate (ml/min)	Hexene	Benzene*	Thiophene**	2-Methylthiophene**	Heptane
100	300	$6.34 \cdot 10^9$	—	$4.76 \cdot 10^{10}$	$2.26 \cdot 10^{11}$	—
	200	$1.09 \cdot 10^{10}$	—	$6.67 \cdot 10^{10}$	$3.17 \cdot 10^{11}$	—
	100	$1.35 \cdot 10^{10}$	—	$1.64 \cdot 10^{11}$	$6.99 \cdot 10^{11}$	—
150	300	$1.52 \cdot 10^{10}$	$3.07 \cdot 10^8$	—	—	—
	200	$2.07 \cdot 10^{10}$	$5.13 \cdot 10^8$	—	—	—
	100	$2.96 \cdot 10^{10}$	$1.97 \cdot 10^9$	—	—	—
200	300	$4.62 \cdot 10^{10}$	$3.44 \cdot 10^9$	—	—	$1.52 \cdot 10^9$
	200	$4.91 \cdot 10^{10}$	$4.34 \cdot 10^9$	—	—	$1.69 \cdot 10^9$
	100	$1.02 \cdot 10^{11}$	$1.23 \cdot 10^{10}$	—	—	$1.72 \cdot 10^9$

* Sensitivity relative to $5.63 \cdot 10^{-6}$ mole.

** Sensitivity relative to the linear range.

TABLE II

DETECTABILITY OF DIFFERENT TYPES OF COMPOUNDS

Calculated as $2 \times \text{noise/sensitivity}$ (mole/sec).

Temperature (°C)	Ozone flow-rate (ml/min)	Hexene	Benzene*	Thiophene**	2-Methylthiophene**	Heptane
100	300	$5.38 \cdot 10^{-9}$	—	$5.67 \cdot 10^{-10}$	$1.19 \cdot 10^{-10}$	—
	200	$3.14 \cdot 10^{-9}$	—	$4.05 \cdot 10^{-10}$	$8.53 \cdot 10^{-11}$	—
	100	$2.53 \cdot 10^{-9}$	—	$1.64 \cdot 10^{-10}$	$3.86 \cdot 10^{-11}$	—
150	300	$2.25 \cdot 10^{-9}$	$1.11 \cdot 10^{-7}$	—	—	—
	200	$1.65 \cdot 10^{-9}$	$6.66 \cdot 10^{-8}$	—	—	—
	100	$1.15 \cdot 10^{-9}$	$1.73 \cdot 10^{-8}$	—	—	—
200	300	$7.40 \cdot 10^{-10}$	$1.00 \cdot 10^{-8}$	—	—	$2.25 \cdot 10^{-8}$
	200	$6.96 \cdot 10^{-10}$	$7.88 \cdot 10^{-9}$	—	—	$2.02 \cdot 10^{-8}$
	100	$3.35 \cdot 10^{-10}$	$2.78 \cdot 10^{-9}$	—	—	$1.99 \cdot 10^{-8}$

* Detectability relative to $5.63 \cdot 10^{-6}$ mole.

** Detectability relative to the linear range.

flow-rate of the ozone mixture was maintained at 100 ml/min for all experiments, except those at 250°, when flow-rates of 300 (D) and 100 ml/min (E) were used.

It can be seen that at 100° (A), the chemiluminescence detector provided a very high olefin selectivity, saturated and aromatic hydrocarbons not being detected. At 150° (B), the aromatic hydrocarbons can be observed, but no signal is obtained for saturated compounds. At 200° (C), all hydrocarbons were detected, but the peaks for the olefins and aromatics were much more intense. At 250° (E) the chromatogram was similar to the flame-ionization detector (F) chromatogram, but the relative peak heights for olefins were approximately twice as large on the chemiluminescence detector as on the flame-ionization detector.

TABLE III
SPECIFICITY FACTORS FOR DIFFERENT TYPES OF COMPOUNDS
(DETECTABILITY A/DETECTABILITY B)

Compound pair (A-B)	Temperature (°C)	Ozone flow-rate (ml/min)		
		100	200	300
Hexene-benzene	100	—	—	—
	150	15.0	40.4	49.5
	200	8.24	11.3	13.4
Hexene-heptane	100	—	—	—
	150	—	—	—
	200	59.3	29.0	30.4
Benzene-heptane	100	—	—	—
	150	—	—	—
	200	7.15	2.57	2.26
Thiophene-hexene	100	12.1	6.12	7.51
	150	—	—	—
	200	—	—	—
2-Methylthiophene-hexene	100	51.8	29.1	35.6
	150	—	—	—
	200	—	—	—

TABLE IV
DETECTOR SENSITIVITY AND DETECTABILITY FOR THIOPHENE
Exponential range.

Temperature (°C)	Ozone flow-rate (ml/min)	Sensitivity (counts·mole ⁻²)	Detectability (mole ² /sec)
100	300	6.49·10 ¹⁷	6.45·10 ⁻⁹
	200	8.19·10 ¹⁷	5.74·10 ⁻⁹
	100	4.52·10 ¹⁸	2.44·10 ⁻⁹

When the flow-rate of the ozone mixture was increased from 100 (E) to 300 ml/min (D), the olefin selectivity increased correspondingly.

These results illustrate the changes in detector selectivity due to variations of the temperature and the flow-rate of the ozone mixture.

CONCLUSIONS

The modified reactor chamber proved to be suitable for the analysis of liquid hydrocarbon samples (aromatic, olefinic and saturated hydrocarbons) and thiophenes, providing good symmetrical chromatographic peaks. For all of the compounds studied linear ranges were obtained, which can be utilized for quantitative analysis.

The detector sensitivity increased with increasing temperature and decreased with increasing flow-rate of the ozone mixture. In addition to being selective for the different types of hydrocarbons, the detector also had a high selectivity for thiophenes.

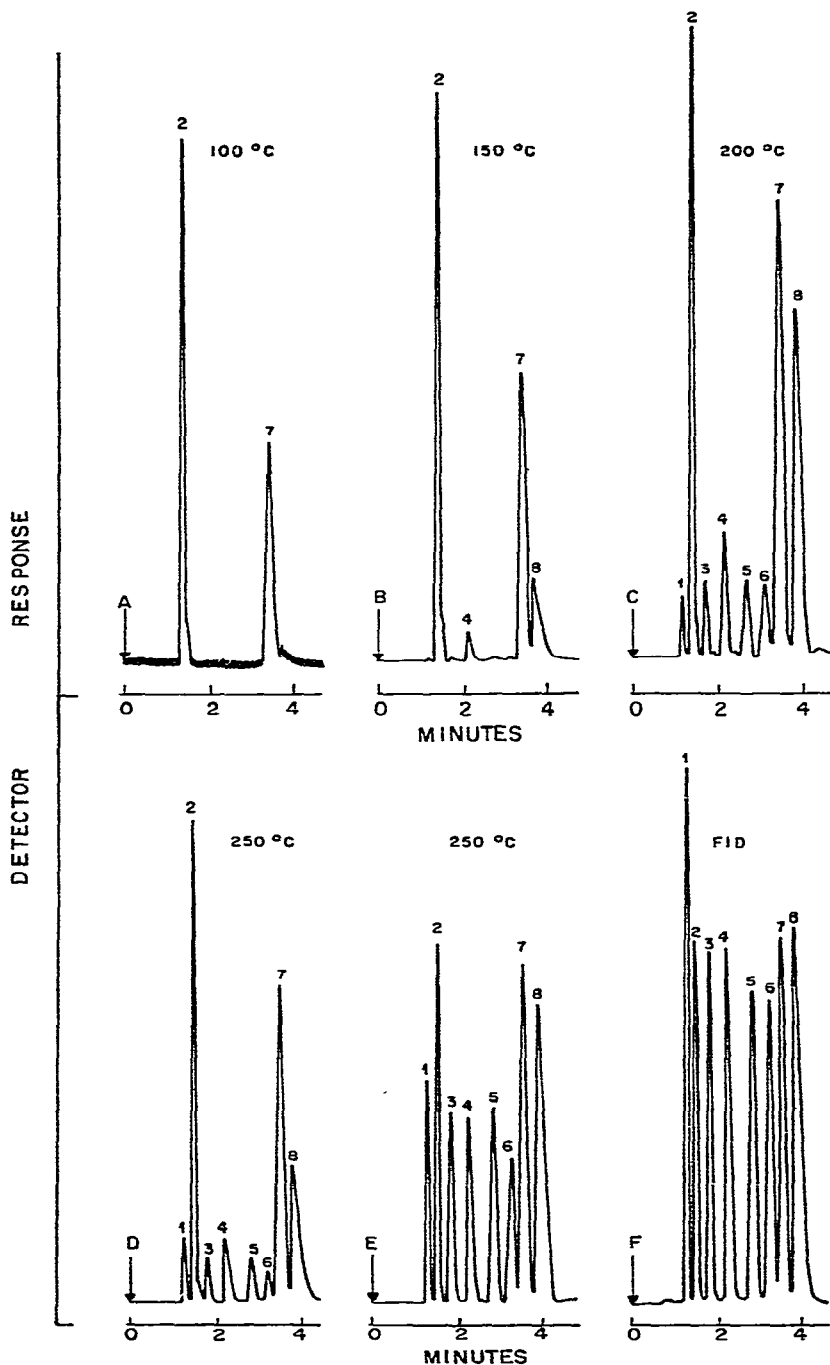


Fig. 6. Hydrocarbon analysis using a chemiluminescence detector with a flow-rate of ozone mixture of 100 ml/min [(A), (B), (C) and (E)] and 300 ml/min (D), and using a commercial FID (F). Column dimensions, 3 m \times 5/64 in. I.D.; packing, 10% diethylene glycol succinate on 100–150-mesh Porasil C; carrier gas, nitrogen at 60 ml/min; column temperature, 127°; injector temperature, 200°. Peaks: 1 = cyclohexane; 2 = 1-hexene; 3 = heptane; 4 = benzene; 5 = 1-octane; 6 = 2,2,5-trimethylhexane; 7 = octene; 8 = toluene.

Further studies using other types of sulphur compounds could possibly enlarge the range of applications of the ozone chemiluminescence detector.

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REFERENCE

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