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# SELECTIVE DETECTOR FOR GAS CHROMATOGRAPHY BASED ON THE CHEMILUMINESCENCE OF OZONE REACTIONS

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## SUMMARY

A selective detector for gas chromatography is described that utilizes the chemiluminescence of ozone reactions as a means of detection through a photon-counting system. The selectivity is provided by variations in the reactivity towards ozone of different classes of compounds and can be adjusted through the detector temperature, which was varied in the range 50–250°. The detector is mass flow-rate sensitive and gives a linear response for different types of hydrocarbons over several orders of magnitude. Its detection limit is frequently at the nanogram level and is temperature dependent, as is its sensitivity. The use of the detector was demonstrated by means of hydrocarbon gas analysis.

## INTRODUCTION

Selective gas chromatographic (GC) detectors are valuable instruments in the analysis of very complex samples. During recent years, several developments have been made, and the most successful detectors are based on the selective determination of hetero-atoms in organic molecules.

Very complex samples, which continue to challenge the analyst, result from cracking processes in the petroleum industry. Usually, large amounts of saturated and unsaturated isomers with very close boiling points are obtained that cannot be resolved satisfactorily even by using high-resolution columns. In these instances, the use of an olefin-selective detector would simplify the analysis considerably.

The development of some selective detectors for unsaturated hydrocarbons has already been reported[1-3], all of which were based on catalytic hydrogenation utilizing the consumption of hydrogen as a means of detection through a double catharometer or an electrochemical cell. However, the selectivities were low[1], and the systems did not prove to be suitable for routine operation[4]. Using hydrogen as carrier gas, Rijnders[4] used an activated carbon filter to retain all hydrocarbons after the hydrogenation reaction, in order to avoid interferences in the thermal conductivity detector that determined the unsaturated compounds through their hydrogen consumption. Also, he used the amount of electricity needed to produce the hydrogen consumed as an additional means of detection. However, the selectivity was affected, because

olefins with shielded double bonds could be hydrogenated only at temperatures at which naphthene dehydrogenation interfered by producing hydrogen and aromatic compounds.

A reaction that has greater possibilities of being used for effective and selective detection is the ozone–olefin reaction. This reaction produces chemiluminescence, which can be easily captured through a light detection system. Such a detector has the advantage of being based on a very fast, non-catalytic and flameless reaction. The utilization of chemiluminescence has already been reported by Nederbragt et al.[5], who used ethylene in order to determine ozone concentrations in radiochemical laboratories. His technique has resulted in a number of commercial instruments used in ozone pollution control.

In this paper, we present the first results obtained with a selective detector that measures the chemiluminescence generated when ozone fed into a reaction chamber reacts with olefins emerging from a GC column. The construction of the detector and its operating characteristics have been studied, and chromatograms with particular emphasis on hydrocarbon selectivity are presented.

## EXPERIMENTAL

### Apparatus

The chemiluminescence apparatus is shown schematically in Fig. 1. It consists of the main components described below.

*Sampling devices.* The injector of the chromatographic system was a Hamilton flash vaporization injector (Hamilton, Whittier, Calif., U.S.A.). The diluted gaseous hydrocarbon mixtures were prepared with an exponential dilution flask (Varian, Palo Alto, Calif., U.S.A.) and were injected with Carle micro-volume valves (Carle Instruments, Fullerton, Calif., U.S.A.).
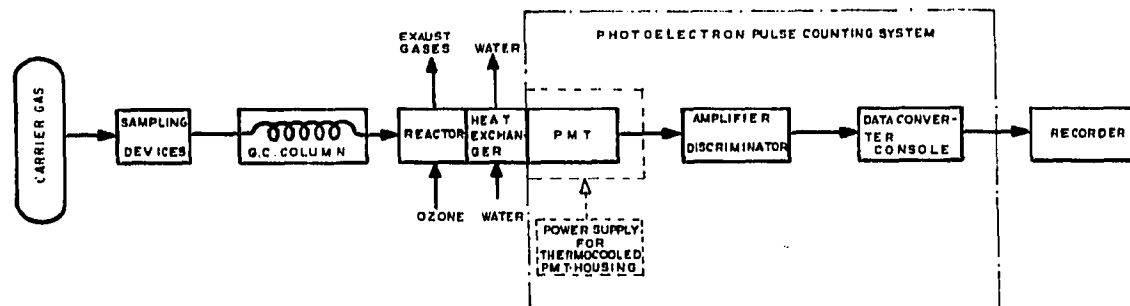


Fig. 1. Schematic diagram of the apparatus.

*Columns.* The GC column used for the investigation of the detector characteristics was a 1 m × 5/64 in. I.D. stainless-steel tube, packed with 10% diethylene glycol (Merck, Darmstadt, G.F.R.) on 100–150 mesh Porasil C (Applied Science Labs., State College, Pa., U.S.A.). The hydrocarbon gas analysis was performed with a 10 m × 5/64 in. I.D. stainless-steel column containing 25% sebaconitrile (Eastman Kodak, Rochester, N.Y., U.S.A.) on 60–80 mesh Chromosorb P.

When temperatures above ambient were required, the chromatographic column was placed in a Haake Model FT constant-temperature circulator bath (Haake, Karlsruhe, G.F.R.).

*Reactor.* The stainless-steel reactor of the detection system is shown in Fig. 2. Basically, it consists of two main parts: the pre-heater and the reaction chamber. The geometry of the chamber influences the detector sensitivity and, therefore, it was previously investigated on a special reactor, the width of which could be varied, the chamber diameter being 2 in. The optimum width was found to be 4 mm. As the sensitivity was not affected when a ring was inserted into the chamber so as to reduce its diameter to 1 in., it was decided to use the smaller dimension in the final reactor.

The function of the pre-heater is to avoid condensation problems, especially when (for selectivity reasons) the reaction chamber is operated at lower temperatures. For the sake of flexibility, it was equipped with an independent temperature regulator.

*Heat exchanger.* The heat exchanger, which is shown in Fig. 2, had the function of protecting the photomultiplier tube (PMT) from high reaction chamber temperatures. It also provided facilities for the inclusion of an optical filter before the PMT. This filter and the quartz window of the reaction chamber were mounted with silicone and asbestos O-rings, respectively.

*Photoelectron pulse-counting system.* The photon-counting system consisted of an EMI 9658-R PMT (Gencon Division, Emitronics, Plainview, N.Y., U.S.A.), mounted in a thermo-cooled photomultiplier housing (Model D 507 T plus Model DP 500 1-2 T power supply, both from Schoeffel Instrument Corp., Westwood, N.J., U.S.A.). With this equipment, the PMT was operated at approximately $-20°$, which is 40° below the temperature of the cooling water.

The output of the PMT was fed into a Model 1120 amplifier/discriminator, and then into a Model 1105 data converter console (SSR Instruments, Santa Monica, Calif., U.S.A.). The PMT was operated at 1100 V and the time constant was 0.1 sec$^{-1}$. The pre-scaler setting was normally 100, which means that only 1 % of the total signal was amplified. The analogue output of the photon counting system was recorded on a Varian A-25 recorder.

The chromatogram obtained by using a flame ionization detector (FID) was run in a Varian Model 1440 chromatograph, which was connected to a Varian A-25 recorder.

*Ozone supply*

Ozone was obtained by means of a Model T-816 laboratory ozonator (Welsbach Corp., Philadelphia, Pa., U.S.A.). The instrument was operated with oxygen (1200 ml/min) at 110 V, resulting in an ozone concentration of approximately 6 % (w/w). Its output was split: 200 ml/min were fed into the reactor and the remainder was vented. The material of the connecting tubings was aluminium and Tygon. Quantitative ozone analyses for the calibration of the generator and detector were carried out by the iodimetric method[6].

*Standards*

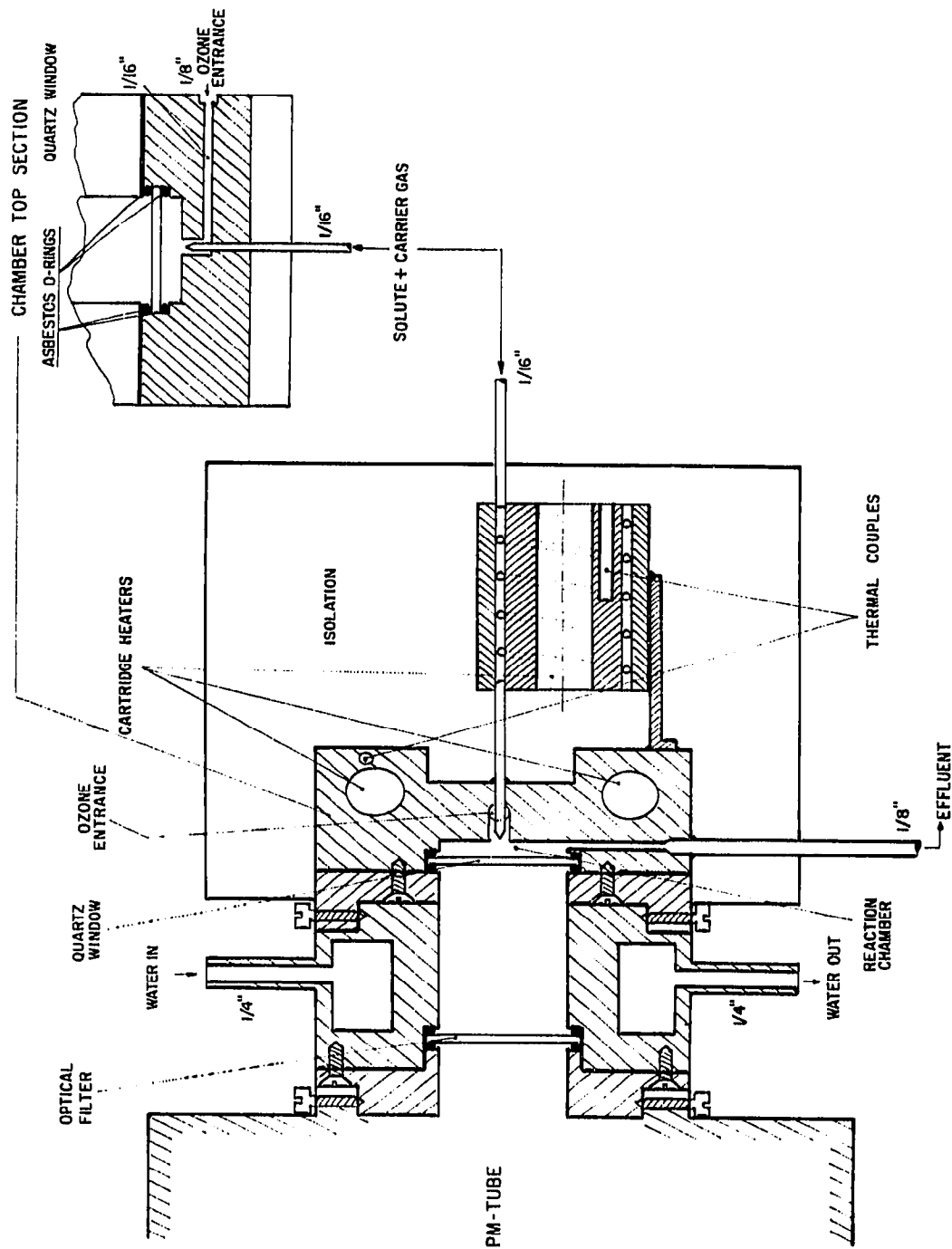The hydrocarbon standards were obtained from Phillips Petroleum (Bartlesville, Okla., U.S.A.).

Fig. 2. Schematic diagram of the reactor and heat exchanger.

## RESULTS AND DISCUSSION

*Detection principles*

The heart of the detector is the reaction chamber, where the solutes, separated by the column, react with ozone in the following simplified manner:

$$\text{Solute} + O_3 \rightarrow A^* + \text{further products}$$
$$A^* \rightarrow A + h\nu$$
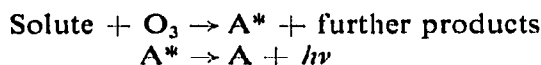
It can be seen that the reaction produces, in addition to other substances, electronically excited species ($A^*$) that emit their excess of energy ($h\nu$) in the visible region of the spectrum. This chemiluminescence was expected to have a relatively low intensity and, therefore, a photon-counting system was chosen for its detection in order to provide suitable sensitivity and detection limits. However, the signal and the noise levels were found to be considerably higher than expected, and therefore a lock-in amplifier would have been appropriate.

The most important feature of this detector is its selectivity, which derives from the variation in the reactivity of ozone towards different classes of compounds. Being a part of the reaction conditions, the detector temperature influences the reactivity of ozone and, surprisingly, proved to be a very simple means of adjusting the detector selectivity. Another possibility of varying the selectivity is through the utilization of chemiluminescent spectral characteristics, which are a function of compound structure.

*Effect of ozone concentration on detector signal*

The function of ozone in the detector was that of a reagent and therefore its concentration had a direct influence on the resulting chemiluminescence. In order to be able to obtain proper detector characteristics, it was important to work with an excess of reagent (ozone). This aspect was investigated by introducing continuously a constant, relatively large amount of ethylene at room temperature into the reactor. A graph of signal *versus* ozone concentration revealed that the detector signal increased exponentially up to an ozone concentration of about 50 mg/l and then remained constant. As the operating conditions of the ozonator conveniently allowed the output of a higher concentration, all of the subsequent experiments were conducted at a concentration of about 60 mg/l.

Another parameter to be investigated was the ozone flow-rate. Flow variations at concentrations above 50 mg/l did not affect the detector. From the splitter, the flow-rate of the ozone stream through the reaction chamber was chosen to be 200 ml/min. This flow-rate was found to be very suitable, because it provided a relatively high gas velocity in the reaction chamber (total volume approximately 1.8 cm$^3$), avoiding condensation problems at low chamber temperatures.

*Effect of temperature on detector signal*

Being based on a chemical reaction, the emission created in the reaction chamber is strongly temperature dependent. Fig. 3 shows how the detector response for different types of hydrocarbon compounds varies with temperature. All of the curves were established with the injection of equimolar amounts of sample and the column
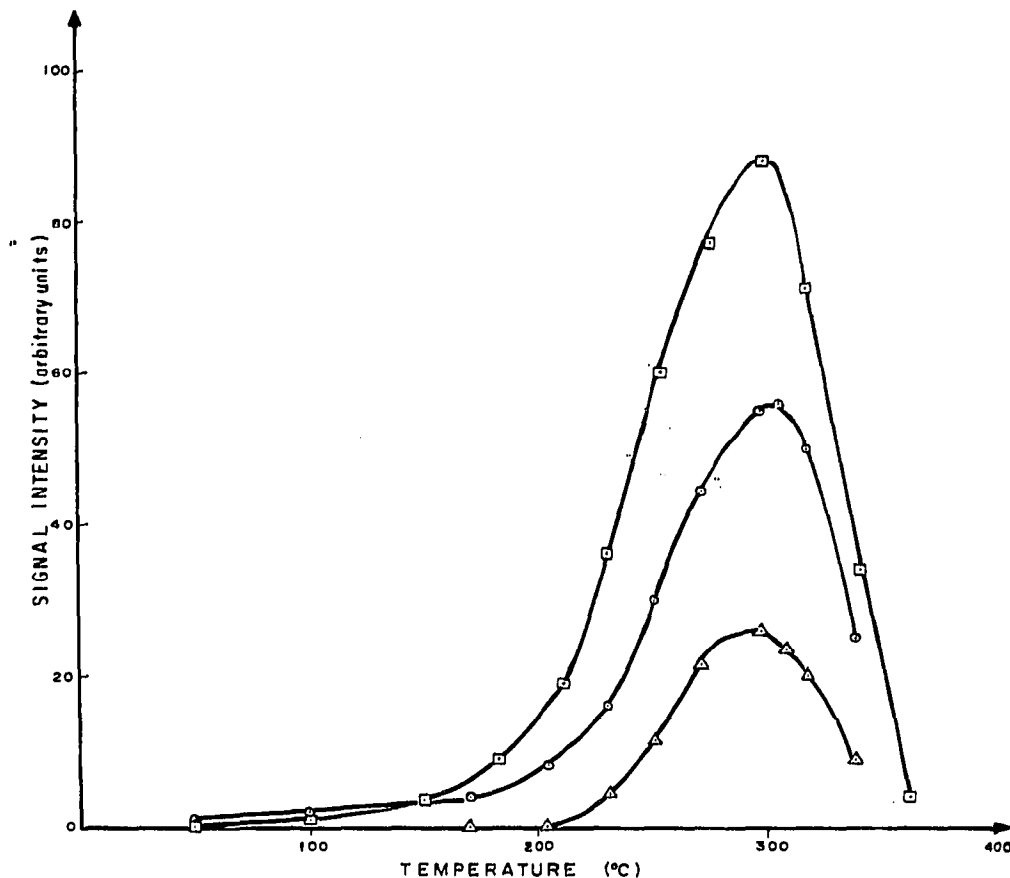
Fig. 3. Detector response for different hydrocarbon gases as a function of the detector temperature. □, Methylacetylene; ⊙, ethylene; △, *n*-butane.

was replaced with a 1 ft. × 1/8 in. O.D. empty stainless-steel tube. The results were characterized by an exponential signal increase up to a temperature of about 300°.

Surprisingly, further temperature increases resulted in a substantial decrease in the signal owing to the effect of temperature on ozone decomposition, represented in Fig. 4. The curve was established by keeping the ozone concentration entering the reaction chamber constant and determining the outlet concentration as a function of the chamber temperature. It can be seen that, up to 150°, the ozone content remained constant (76 mg/l). However, further temperature increases led to ozone decomposition, its concentration decreasing to 6 mg/l at 300°.

The effect of temperature on the detector signal thus operates in two opposing directions. Temperature increase enhances the emission intensity, but simultaneously diminishes the signal through the decomposition of ozone. In Fig. 3, up to about 300° the former effect predominates, but at higher temperatures ozone decomposition starts to predominate.

A more complete investigation of the overall effect of temperature was carried
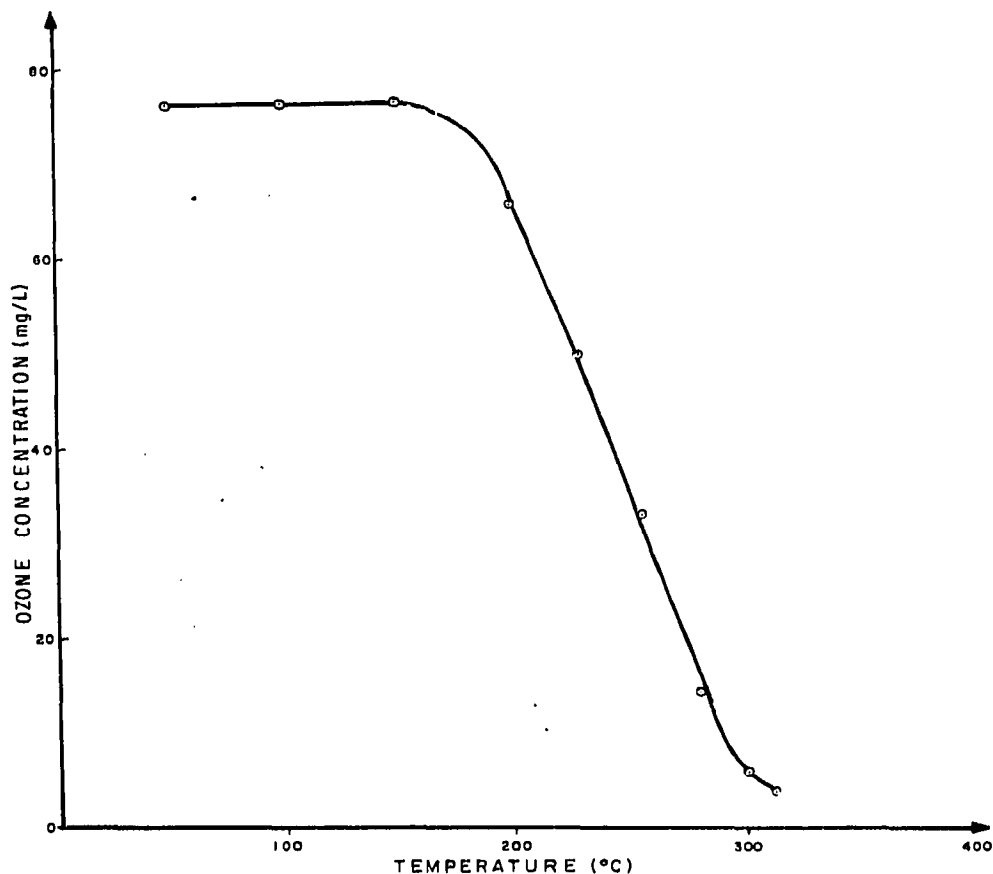
Fig. 4. Ozone decomposition with increase in temperature.

out with ethylene at three different ozone concentrations and four different tempera-
tures. For practical reasons, the empty stainless-steel tube was used instead of the
chromatographic column. The results are shown in Fig. 5. As has been observed
before, the detector sensitivity increased as the ozone concentration and temperature
increased. Further, the triplets of curves obtained at each temperature changed from
linear at 100° to non-linear at 300°. At intermediate temperatures (200 and 250°), the
linearity within the triplets increased with ozone concentration. Consequently, the
observed non-linearity was the result of the decrease in ozone concentration caused
by its decomposition at higher temperatures.

*Detector characteristics*

Calculated values for the detector sensitivity, detectability and specificity are
presented in Tables I–III, respectively, as a function of temperature. They are based
on experimental data obtained with the diethylene glycol column, the efficiency of
which varied between 640 theoretical plates for ethylene and 1150 for propane.

Again, the results can easily be understood on the basis of a chemical reaction
of ozone. All three characteristics are affected by variations in the reactivity of dif-
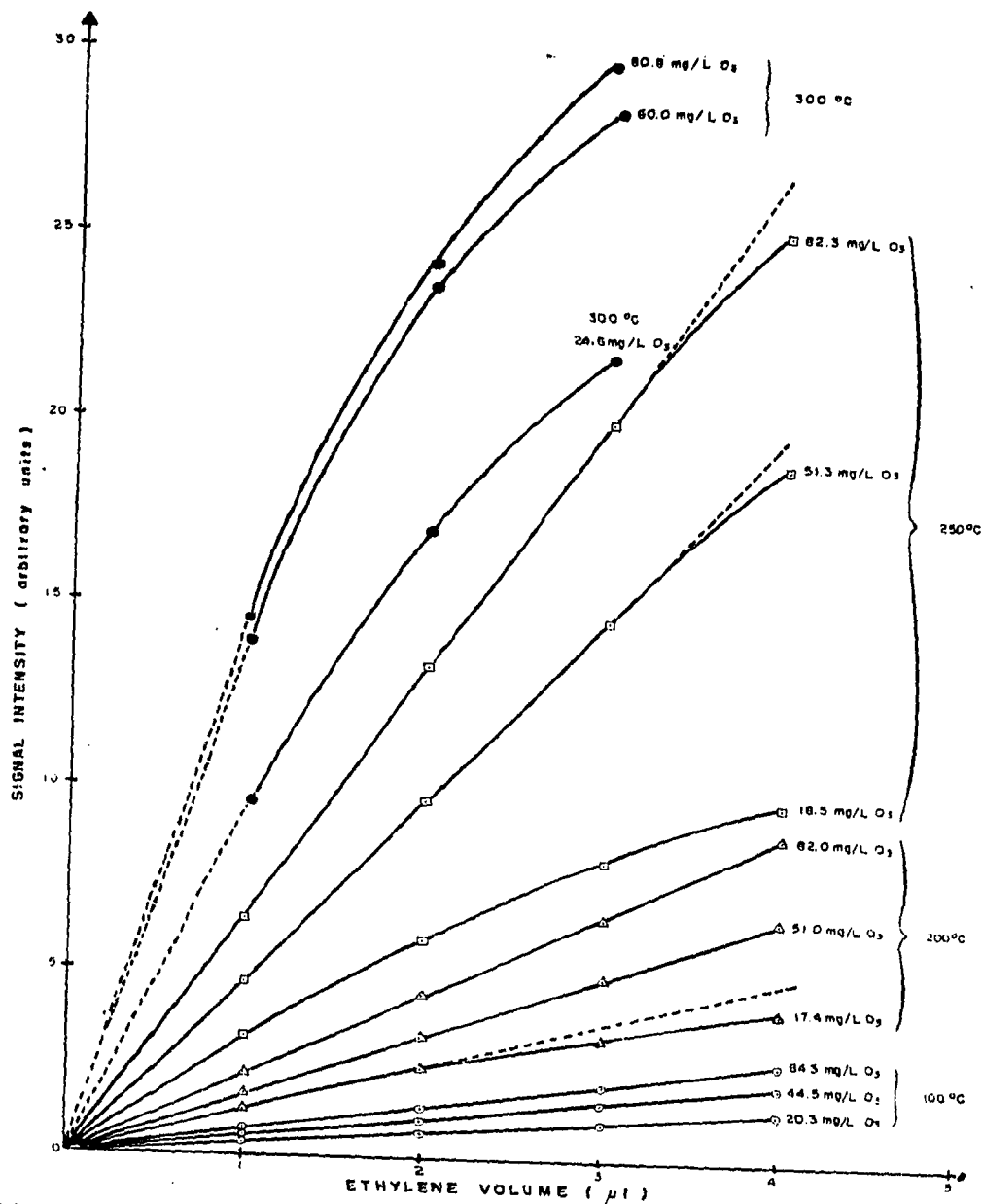
Fig. 5. Effect of temperature and ozone concentration on detector sensitivity and linearity.

ferent classes of compounds towards ozone and, further, by the reaction conditions (detector temperature). At relatively low temperatures, the reactivity of propane and benzene towards ozone is very low and, consequently, low sensitivities and detectabilities were observed. However, they improved rapidly at temperatures above 150°, and at 250° they reach the same order of magnitude as those of ethylene, acetylene and propadiene. Based on their high reactivity towards ozone, these three compounds

TABLE I

DETECTOR SENSITIVITY FOR DIFFERENT TYPES OF HYDROCARBONS

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

| Temperature (°C) | Propane | Benzene | Ethylene | Acetylene | Propadiene |
|---|---|---|---|---|---|
| 50 | — | — | $2.9 \cdot 10^{10}$ | $4.3 \cdot 10^{10}$ | $1.3 \cdot 10^{11}$ |
| 100 | — | $1.0 \cdot 10^{9}$ | $1.4 \cdot 10^{11}$ | $1.7 \cdot 10^{11}$ | $6.9 \cdot 10^{11}$ |
| 150 | $2.2 \cdot 10^{6}$ | $1.2 \cdot 10^{10}$ | $2.4 \cdot 10^{11}$ | $5.7 \cdot 10^{11}$ | $1.2 \cdot 10^{12}$ |
| 175 | $3.8 \cdot 10^{9}$ | $4.1 \cdot 10^{10}$ | $3.4 \cdot 10^{11}$ | $9.0 \cdot 10^{11}$ | $1.6 \cdot 10^{12}$ |
| 200 | $3.8 \cdot 10^{10}$ | $1.2 \cdot 10^{11}$ | $6.2 \cdot 10^{11}$ | $1.8 \cdot 10^{12}$ | $2.2 \cdot 10^{12}$ |
| 225 | $3.0 \cdot 10^{11}$ | $3.3 \cdot 10^{11}$ | $1.3 \cdot 10^{12}$ | $2.9 \cdot 10^{12}$ | $3.4 \cdot 10^{12}$ |
| 250 | $1.2 \cdot 10^{12}$ | $7.4 \cdot 10^{11}$ | $2.3 \cdot 10^{12}$ | $3.9 \cdot 10^{12}$ | $5.0 \cdot 10^{12}$ |

TABLE II

DETECTABILITY FOR DIFFERENT TYPES OF HYDROCARBONS

Calculated as $2 \times$ noise/sensitivity (moles/sec).

| Temperature (°C) | Propane | Benzene | Ethylene | Acetylene | Propadiene |
|---|---|---|---|---|---|
| 50 | — | — | $1.5 \cdot 10^{-9}$ | $1.1 \cdot 10^{-9}$ | $3.3 \cdot 10^{-10}$ |
| 100 | — | $4.1 \cdot 10^{-8}$ | $2.9 \cdot 10^{-10}$ | $2.4 \cdot 10^{-10}$ | $6.0 \cdot 10^{-11}$ |
| 150 | $1.8 \cdot 10^{-5}$ | $3.7 \cdot 10^{-9}$ | $1.8 \cdot 10^{-10}$ | $7.3 \cdot 10^{-11}$ | $3.4 \cdot 10^{-11}$ |
| 175 | $1.1 \cdot 10^{-8}$ | $1.0 \cdot 10^{-9}$ | $1.2 \cdot 10^{-10}$ | $4.7 \cdot 10^{-11}$ | $2.6 \cdot 10^{-11}$ |
| 200 | $1.1 \cdot 10^{-9}$ | $3.4 \cdot 10^{-10}$ | $6.8 \cdot 10^{-11}$ | $2.3 \cdot 10^{-11}$ | $1.9 \cdot 10^{-11}$ |
| 225 | $1.4 \cdot 10^{-10}$ | $1.3 \cdot 10^{-10}$ | $3.3 \cdot 10^{-11}$ | $1.4 \cdot 10^{-11}$ | $1.2 \cdot 10^{-11}$ |
| 250 | $3.4 \cdot 10^{-11}$ | $5.7 \cdot 10^{-11}$ | $1.8 \cdot 10^{-11}$ | $1.1 \cdot 10^{-11}$ | $8.2 \cdot 10^{-12}$ |

TABLE III

SPECIFICITY FACTORS FOR DIFFERENT TYPES OF HYDROCARBONS (DETECTABILITY A/DETECTABILITY B)

| Compound pair (A/B) | Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 50 | 100 | 150 | 175 | 200 | 225 | 250 |
| Propane/benzene | — | — | $2.8 \cdot 10^{3}$ | 6.1 | 1.8 | 0.6 | 0.3 |
| Propane/ethylene | — | — | $1.6 \cdot 10^{5}$ | $1.4 \cdot 10^{4}$ | 26 | 6.7 | 2.9 |
| Propane/acetylene | — | — | $4.2 \cdot 10^{5}$ | $4.1 \cdot 10^{4}$ | 82 | 16 | 5.4 |
| Propane/propadiene | — | — | $5.9 \cdot 10^{5}$ | $4.7 \cdot 10^{4}$ | 64 | 12 | 4.5 |
| Benzene/ethylene | — | $3.9 \cdot 10^{2}$ | 59 | 24 | 14 | 11 | 11 |
| Benzene/acetylene | — | $5.1 \cdot 10^{2}$ | $1.5 \cdot 10^{2}$ | 66 | 45 | 27 | 20 |
| Benzene/propadiene | — | $1.3 \cdot 10^{3}$ | $2.1 \cdot 10^{2}$ | 76 | 36 | 20 | 17 |
| Ethylene/acetylene | 1.6 | 1.3 | 2.6 | 2.8 | 6.3 | 2.5 | 1.8 |
| Ethylene/propadiene | 3.2 | 3.4 | 3.5 | 3.2 | 2.5 | 1.9 | 1.5 |
| Acetylene/propadiene | 2.0 | 2.6 | 1.4 | 1.1 | 0.79 | 0.75 | 0.85 |

showed high sensitivity and detectability even at low temperatures. The values improved according to the degree of unsaturation.

Contrary to the specificity factors, the sensitivities and detectabilities were calculated on a molar instead of a gram basis. This expresses better the results obtained as a function of compound bond characteristics.

Specificity factors, shown in Table III, are a measure of the detector selectivity. The factors represent detectability ratios and were obtained from the data in Table II. Consequently, the effect of temperature was the same as that for the other characteristics. Very high factors resulted from pairs of compounds that involved propane at low temperatures. They decreased with increasing temperature and differed by one order of magnitude at 250°. Pairs of compounds that involved benzene also had high factors at lower temperatures, remaining relatively high at 250°. The detector selectivity with ethylene, acetylene and propadiene was small over the whole temperature range.

The type of detector response was investigated according to the method of Halász[7], and it was found to be mass flow-rate dependent.

Another detector characteristic investigated was the linearity. Diluted hydrocarbon gas mixtures were prepared by using an exponential dilution flask and were injected into the diethylene glycol column with Carle micro-volume sample valves at detector temperatures of 100 and 250°. The resulting logarithmic plots of the detector peak area response *versus* amount of sample are shown in Fig. 6. Each curve had a slope of 1.0. At 250°, they were linear up to about 1 μg of sample. Unfortunately, the upper limit of the linear range could not be reached at 100°, because a suitable sample valve was missing. However, injections of undiluted ethylene and acetylene have shown that the linear range extends at least one more order of magnitude (to
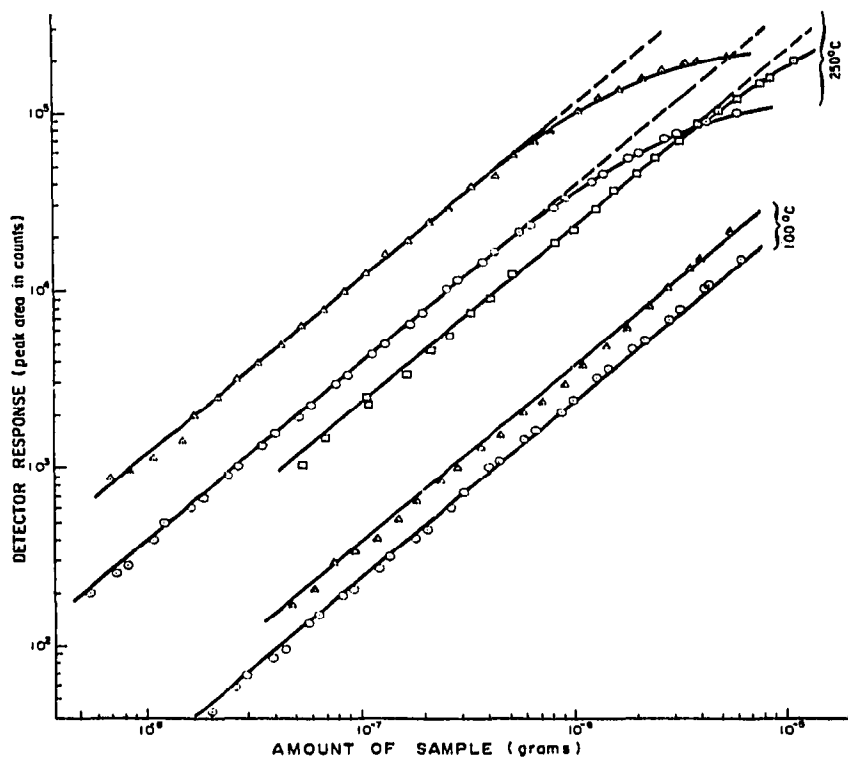


Fig. 6. Detector linearity. Area response as a function of amount of sample. △, Acetylene; ○, ethylene; ▯, n-butane.
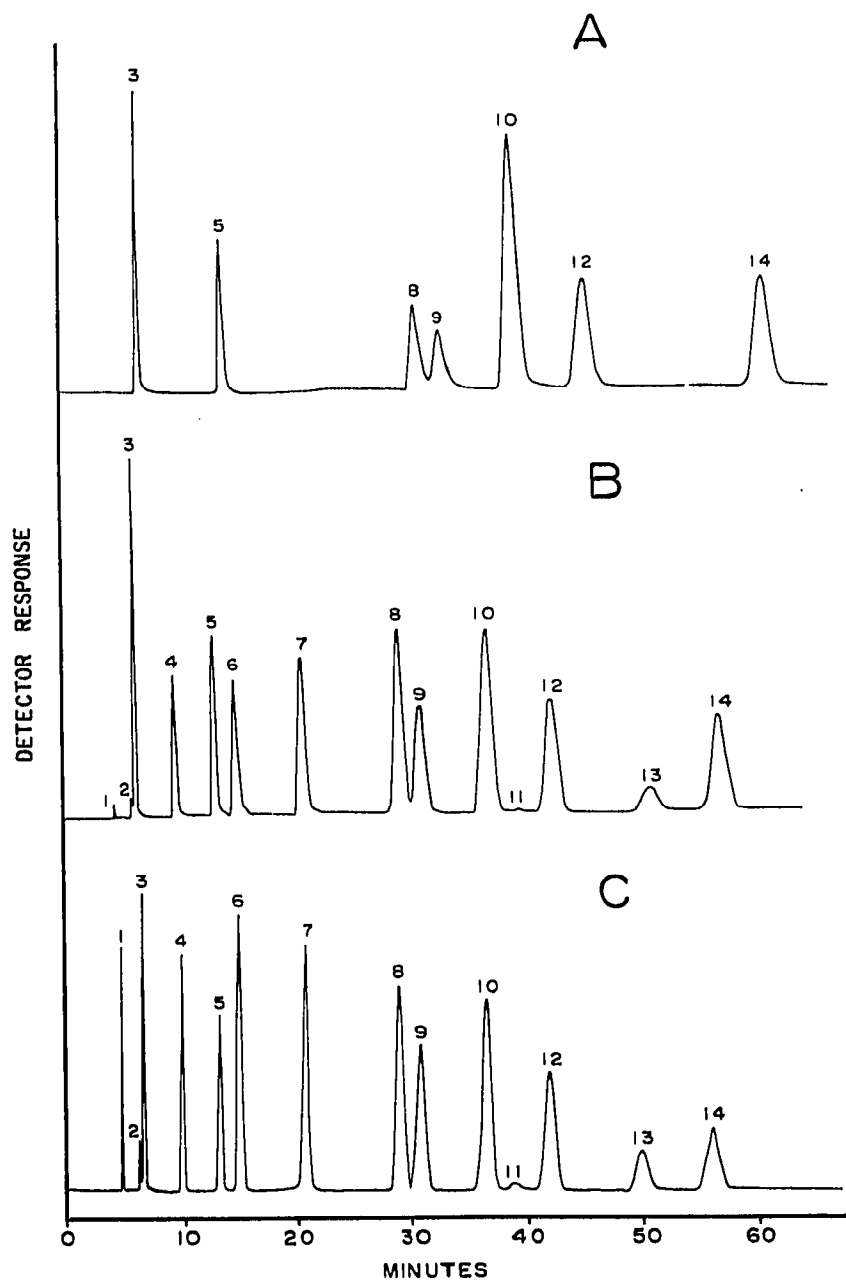
Fig. 7. Hydrocarbon analysis using a chemiluminescence detector at 100° (A) and 250° (B) and a commercial FID (C). Peaks: 1 = methane; 2 = ethane; 3 = ethylene; 4 = propane; 5 = propene; 6 = isobutane; 7 = *n*-butane; 8 = butene-1; 9 = isobutene; 10 = *trans*-butene-2; 11 = isopentane; 12 = *cis*-butene-2; 13 = *n*-pentane; 14 = butadiene-1,3.

0.1 mg) at this temperature. The detector thus provided useful linear ranges, which may serve as a good basis for quantitative work.

## Detector noise and background levels

Using a pre-scaler and time constant settings of 100 and 0.1 $sec^{-1}$, respectively, the baseline noise was usually about 20 counts·$sec^{-1}$ at a detector temperature of 100° and about 30 counts·$sec^{-1}$ at 250°.

Up to 200°, the total background was relatively low and amounted to about 40 counts·$sec^{-1}$. At higher temperatures, it increased rapidly, reaching 2500 counts·$sec^{-1}$ at 250° and 74,000 counts·$sec^{-1}$ at 340°. This high background was caused mainly by ozone decomposition up to 280°. However, at 340°, its contribution to the total background decreased to about 10%. From these results, it can be seen that the operation of the detector was not affected, because the extremely high backgrounds occurred outside the working temperature range.

## Applications

The ozone chemiluminescence detector (OCD) was applied to the analysis of a selected $C_1$–$C_5$ hydrocarbon gas mixture, containing olefins and saturated hydrocarbons. Two runs were made at detector temperatures of 100 and 250°, and the results were compared with those obtained by using a FID.

The chromatograms are presented in Fig. 7. It can be seen that at 100°, the OCD provided very high olefin selectivity, because none of the saturated compounds appeared in the chromatogram. At 250°, the selectivity changed considerably: all compounds were detected, but with different intensities. A comparison of the chromatograms B and C presented some interesting aspects related to the peak intensities. Firstly, the FID intensity for methane was about 16 times higher than the OCD intensity at 250°. Obviously, the absence of C–C bonds in methane decreased its reactivity towards ozone. Further, the relative peak heights for saturated compounds were approximately twice as large on the FID as on the OCD, while for olefins they were about the same. These results show that even at 250°, the OCD responded preferentially towards unsaturated compounds.

Recently, the applications of the OCD were extended to heavier hydrocarbon samples (aromatic, olefinic and saturated compounds up to $C_8$). The detector functioned well at relatively high temperatures, but peak tailing occurred below 150°. This tailing was apparently caused by adsorption of compounds on the surfaces in the reaction chamber, which was favoured by temperature gradients. In order to overcome these problems, the construction of a new reaction chamber was initiated in order to improve the thermal and flow characteristics.

## ACKNOWLEDGEMENTS

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