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Determination of reactive hydrocarbons by capillary gas chromatography with the reduction gas detector

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Abstract

The reduction gas detector has been used successfully for the capillary GC determination of C_2–C_6 alkenes and isoprene. The detection limits have been improved by using a capillary GC column. The peak shapes for hydrocarbons above C_6 (benzene, toluene, *p*-xylene, *o*-xylene, α-pinene and β-pinene) are very broad and tailing due to their slow and incomplete reactions with HgO at the maximum temperature (300°C) achievable with the present reduction gas detector. If the HgO bed temperature of the detector could be increased, the system might be applicable to the detection of higher-molecular-mass compounds.

1. Introduction

Few hydrocarbons are toxic in their own right at the concentrations found in the ambient atmosphere. Their main contribution to air pollution stems from their atmospheric degradation to ozone, peroxyacetyl nitrate (PAN), hydrogen peroxide and other secondary air pollutants. Because of their extremely low concentrations [volume mixing ratios of 10^{-9} (ppb, v/v), or 10^{-12} (ppt, v/v)], hydrocarbons are difficult to monitor at ambient concentration levels. Development of more sensitive detection systems for hydrocarbons, compatible with gas chromatographic (GC) separation methods, is therefore an urgent priority. Since the more reactive hydrocarbons (e.g., alkenes) have much higher potentials for ozone formation than the non-reactive hydrocarbons (e.g., alkanes), the priority in atmospheric monitoring programmes which focus on photochemical ozone production is therefore the quantitation of the reactive volatile organic compounds (VOCs), rather than of the non-reactive species. Under some circumstances it would therefore be advantageous to utilize a detection system that has enhanced sensitivity towards alkenes but is relatively insensitive to alkanes and other less reactive VOC species. This would result in a less complex chromatogram than is obtained with other universal detectors, for example the flame ionization detector, and so simplify peak identification.

The reduction gas detector was originally developed for detecting the reducing gases CO and H_2 [1]. It has also been used for the detection of acetaldehyde and acetone [2] and of isoprene. Recently, the reduction gas detection

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(RGD) response to the reactive hydrocarbons has been investigated using GC with a packed column [3]. It was shown that RGD is considerably more sensitive to alkenes than is flame ionization detection (FID), and it has much greater sensitivity to alkenes than alkanes.

Because the RGD system was designed for the simple reducing gases, the detector is engineered for use with packed GC columns. However, in order to use RGD for environmental analysis, it is very desirable that it should be compatible with high-resolution capillary GC columns. This would allow advantage to be taken of the high resolving power of capillary columns and may also improve the detection limits of the detector. One of the disadvantages of using packed GC columns is that the analysis has to be carried out isothermally, since RGD is very sensitive to changes in the carrier gas flow-rate. This is adequate for the analysis of simple reducing gases (e.g., H_2, CO), but prevents the separation of compounds with a wide range of boiling points (e.g., C_2–C_{10} hydrocarbons). Moreover, because the carrier gas flow-rate through the capillary column is only a small part of that of the make-up gas ($<0.5\%$), the total carrier gas flow-rate will not change significantly when the GC oven temperature changes. Thus, temperature programming may be employed for the analysis of hydrocarbons when using a capillary GC column.

In this work, a make-up gas line was made in order to render RGD compatible with capillary GC columns. The response of RGD to alkenes and other hydrocarbons was investigated using GC with four different capillary columns.

2. Experimental

2.1. Principle of the reduction gas detector

The principle of operation of the reduction gas detector has been described elsewhere [3,4]. Briefly, it depends upon the reduction of solid mercuric oxide by a reducing gas X on a heated bed:

$$X + HgO(solid) \rightarrow XO + Hg(vapour) \quad (1)$$

The resultant mercury vapour concentration is directly proportional to the inlet gas concentration and is quantitatively detected by means of an ultraviolet photometer located immediately downstream of the reaction bed.

2.2. Analytical system

GC measurements were made using a Hewlett-Packard 5890 Series II gas chromatograph fitted with the reduction gas detector. The carrier gas used was helium. The reduction gas detector employed in this work was an RGD-2 (Trace Analytical, Menlo Park, CA, USA). Four different capillary columns were used in this work to investigate the RGD responses to different hydrocarbons: (i) porous-layer open tubular (PLOT; Al_2O_3/KCl), 50 m × 0.32 mm (Chrompack); (ii) Ultra 2 (cross-linked 5% phenyl methylsilicone), 25 m × 0.2 mm, film thickness (d_f) 0.33 μm (Hewlett-Packard); (iii) HP-1 (cross-linked methylsilicone gum), 10 m × 0.53 mm, d_f 2.65 μm (Hewlett-Packard); (iv) HP-1 (cross-linked methylsilicone gum), 25 m × 0.32 mm, 1.05 μm film thickness (Hewlett-Packard).

A make-up gas line (stainless-steel tube, 1/8 in. I.D.; 1 in. = 2.54 cm) was made in order to use the RGD system with the capillary GC. A catalytic combustion filter was used in conjunction with an organic–water vapour trap (molecular sieve) for carrier gas purification. An uncoated fused-silica capillary (15 cm × 0.53 mm) was used as the transfer line and was connected to the capillary GC column by a glass press-fit connector (Hewlett-Packard).

Sample vapours were injected into the carrier gas stream by means of a gas-tight syringe via a Chrompack TCT injector. The injected vapours were then carried by helium gas through a heated (220°C) empty Perkin-Elmer stainless-steel tube to a coated (CP-Sil 8CB, $d_f = 5$ μm) fused-silica capillary trap [5] which was cooled by liquid nitrogen. After sample concentration, the trap was flash-heated to 220°C at 15°C/s for 1

min, and the trapped vapours injected onto the GC capillary column in the splitless mode. A schematic diagram of the whole TCT–GC–RGD system is shown in Fig. 1.

2.3. Analytes

The RGD responses of C_2–C_6 alkenes, isoprene, benzene, toluene, *p*-xylene, *o*-xylene, α-pinene and β-pinene were investigated. A 15 ppm (v/v) Scotty standard calibration mixture (Chrompack) was used as the standard for C_2–C_6 alkenes. Dilutions of these standards were made by injecting known volumes of vapours into a 1-l glass flask. Mixtures of isoprene, benzene, toluene, *p*-xylene, *o*-xylene, α-pinene and β-pinene vapours were prepared using the static dilution bottle method [6,7].

3. Results and discussion

3.1. The RGD responses to alkenes and other hydrocarbons

RGD has been shown to be considerably more sensitive and selective for the detection of C_2–C_6 alkenes than the commonly used FID [3]. In order to investigate if RGD can be used for the detection of other hydrocarbons, the RGD responses to C_5–C_{10} hydrocarbons were studied using different capillary GC columns.

Fig. 2a shows GC–RGD responses to these C_5–C_{10} hydrocarbons from the Ultra 2 capillary column. It can be seen that the peak of isoprene is relative sharp with slight tailing, while peak tailing is a severe problem for all the other hydrocarbons, especially for the heavier ones. This may be due to the extremely low carrier gas

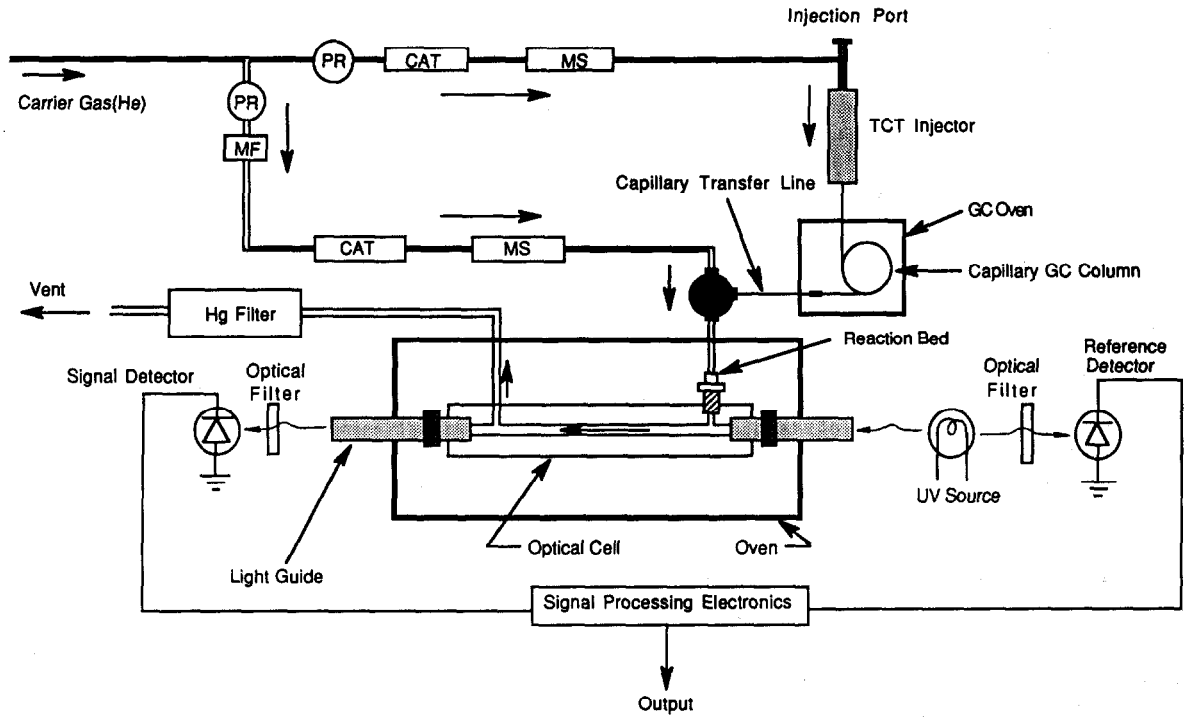

Fig. 1. Schematic diagram for the TCT–GC–RGD system. MS = Molecular sieve; CAT = catalytic combustion filter; MF = mass flow regulator; PR = pressure regulator.

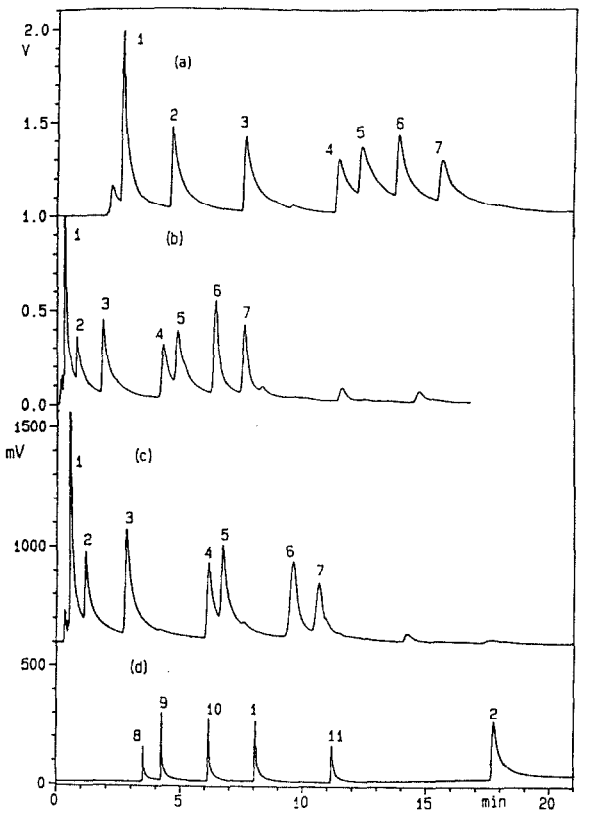

Fig. 2. GC–RGD chromatograms of hydrocarbons. TCT conditions: desorption temperature 220°C (2 min), injection temperature 210°C (1 min), cold trap temperature −190°C. (a) Ultra 2 column (25 m × 0.2 mm), temperature programme 35°C (3 min) to 200°C at 5°C/min, flow-rate through HgO 23 ml/min. (b) HP-1 column (10 m × 0.53 mm), temperature programme as in (a), flow-rate through HgO 35 ml/min. (c) HP-1 column (25 m × 0.32 mm), temperature programme as in (a), flow-rate through HgO 40 ml/min. (d) PLOT column (50 m × 0.32 mm), temperature programme 160°C (8 min) to 180°C at 3°C/min, flow-rate through HgO 28 ml/min. Peaks: 1 = isoprene; 2 = benzene; 3 = toluene; 4 = *p*-xylene; 5 = *o*-xylene; 6 = α-pinene; 7 = β-pinene; 8 = propene; 9 = 1-butene; 10 = 1-pentene; 11 = 1-hexene.

(He) flow-rate through the capillary column (< 1 ml/min) because the Ultra 2 is a very-narrow-bore (I.D. 0.2 mm) capillary. In order to investigate if a higher flow-rate of carrier gas through the column can improve the peak shape or not, two capillary columns with wide bores were used.

The flow-rate of carrier gas through the 25 m × 0.32 mm I.D. HP-1 capillary is about 3 ml/min. While the 10 m × 0.53 mm I.D. HP-1 is a wide-bore capillary, its performance is similar to a packed GC column. The flow-rate through this column can be higher than 30 ml/min depending on the head pressure. The RGD responses to the C_5–C_{10} hydrocarbons from these two capillary columns are shown in Fig. 2b and c. It can be seen that the peak shapes for these hydrocarbons were indeed improved, but not significantly. Moreover, these peaks are still very broad despite the high resolving power of the capillary used. The effect of make-up gas flow-rates (from 20 to 50 ml/min) on the peak shape was also investigated, and it was found that different make-up gas flow-rates can only change the retention times and the sensitivity, but the peak shapes cannot be improved even at higher make-up gas flow-rates.

Because RGD was designed for the detection of simple reducing gases, the HgO bed temperatures can only be adjusted between 200 and 300°C. Thus, the peak shapes (broad, tailing) of these hydrocarbons with RGD may be due to their slow and incomplete reaction (1) even at the highest HgO bed temperature achievable. In order to check this possibility, the RGD responses to C_2–C_6 alkenes, isoprene and benzene were investigated using a PLOT capillary column. A typical chromatogram is shown in Fig. 2d.

It can be seen that the peak shapes for C_3–C_6 alkenes (ethene cannot be trapped) and isoprene are relative sharp with slight tailing. This may be due to the sudden change of temperature from 160°C in the GC oven to the room temperature to which part of the transfer line (ca. 10 cm) was exposed. It is expected that the peak shapes will be improved further if the transfer line is heated. However, the peak shape of benzene is still broad and tailing as observed above with the other capillary columns. This may confirm that the broad and tailing peaks for those $C \geq 6$ hydrocarbons from RGD are due to the slow and incomplete reaction (1). It is suggested that the temperature range of the HgO bed should be broadened in order to detect heavier compounds with this detector.

It can also be seen from all the chromatograms in Fig. 2 that the baseline drift with increasing GC oven temperatures was eased significantly with the capillary columns. This is in marked contrast to the very significant baseline drift that was observed with a temperature-ramped packed column.

3.2. The response linearity of the capillary GC–RGD system

In order to investigate the response linearity of the capillary GC–RGD system to different hydrocarbons, different amounts of C_2–C_6 alkenes, isoprene and benzene vapours were injected onto the GC–RGD system with the PLOT capillary column. Their responses in both area and height counts were plotted against the mass of hydrocarbons injected, and the results shown in Figs. 3–8.

It can be seen that the linearity ranges of the RGD responses generally increase with the carbon number of the hydrocarbon, from ca. 0.3 ng for propene to ca. 2.0 ng for benzene. This is because the linearity range of the RGD responses depends very much on the peak height, rather than peak area. It can be seen from Figs. 3–8 that generally the RGD responses will begin to deviate when the peak height is greater than 500–600 mV. Although a capillary GC column was used, peak tailing and broadening still occurred due to the problems of the detector itself. Thus, for the lighter hydrocarbons which appear at the beginning of the chromatogram, their peaks will be very sharp, and their linearity range will be very narrow; while the peaks of the relatively heavier hydrocarbons will be broader, and their linear range will be wider. Therefore, although the capillary columns can be used for environmental analysis, the linearity range of RGD will be narrow.

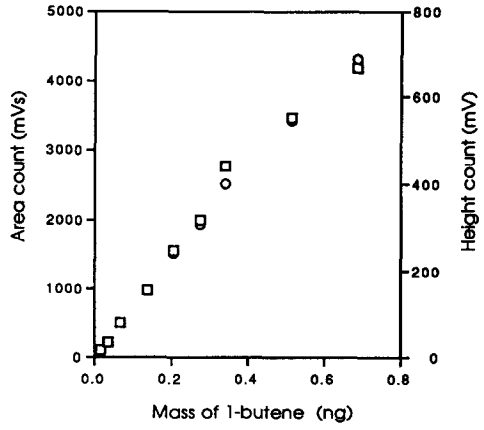

Fig. 4. Linearity of the RGD responses to 1-butene. □ = Height; ○ = area.

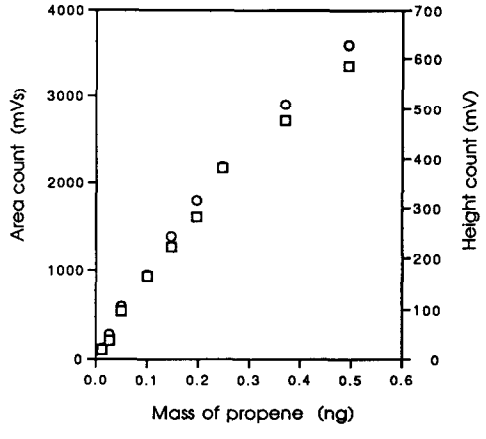

Fig. 3. Linearity of the RGD responses to propene. □ = Height; ○ = area.

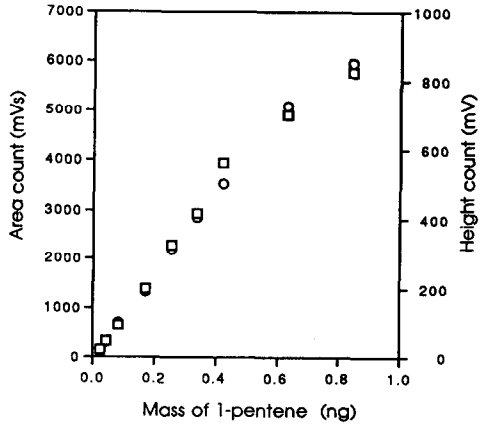

Fig. 5. Linearity of the RGD responses to 1-pentene. □ = Height; ○ = area.

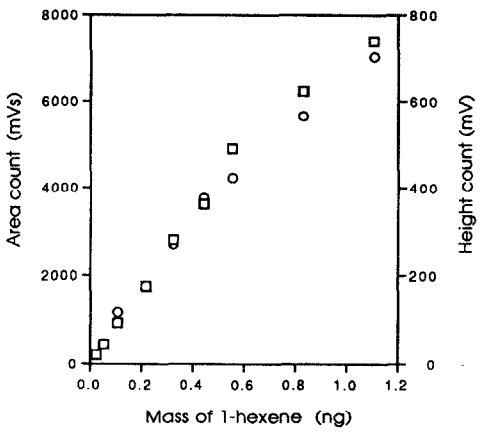

Fig. 6. Linearity of the RGD responses to 1-hexene. □ = Height; ○ = area.

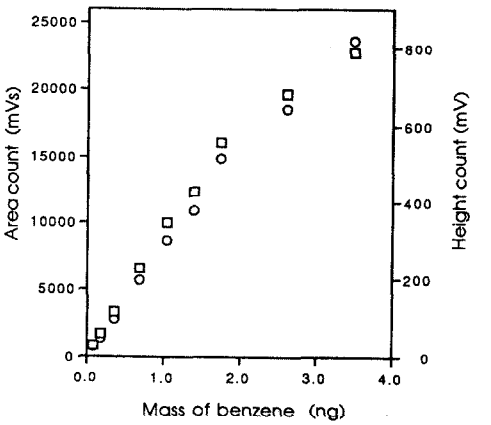

Fig. 8. Linearity of the RGD responses to benzene. □ = Height; ○ = area.

3.3. Detection limits of the capillary GC–RGD system for hydrocarbons

The minimum detectable amounts of alkenes, isoprene and benzene using the capillary GC–RGD system were determined, based on a signal-to-noise ratio of 2, and the results shown in Table 1.

It can be seen from Table 1 that the detection limits have been improved indeed by using the capillary GC column, but not substantially because peak tailing is still a problem even when a capillary column is used, and the signals are much more noisy when using thermal desorption injection than when using direct injection with syringe.

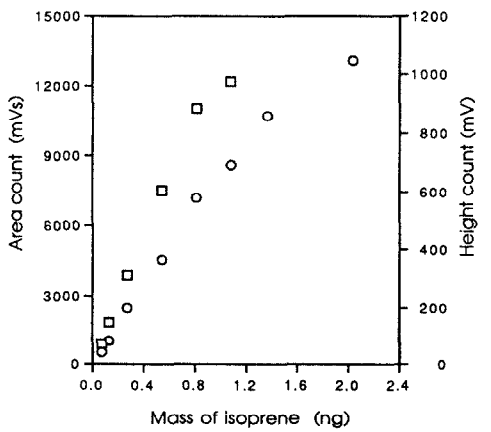

Fig. 7. Linearity of the RGD responses to isoprene. □ = Height; ○ = area.

4. Conclusions

RGD, which has been applied to the quantitation of hydrocarbons separated with a packed column, has been further developed for detecting reactive hydrocarbons using capillary GC. This capillary GC–RGD system can be successfully used for the analysis of C_3–C_6 alkenes and isoprene using a 50-m PLOT capillary column. The detection limits have been improved by using the capillary GC column, but not substantially. It is expected that they can be improved further by heating the transfer line and designing a micro-RGD system. The peak shapes for hydrocarbons $\geq C_6$ are broad and tail severely,

Table 1
Detection limits of the capillary GC–RGD systems for hydrocarbons.

Compounds	Detection limits (ng)
Propene	0.006
1-Butene	0.008
1-Pentene	0.010
1-Hexene	0.014
Isoprene	0.010
Benzene	0.030

due to their slow and incomplete reactions with HgO even at the maximum HgO bed temperature (300°C) achievable with the present RGD system. It is suggested that the HgO bed temperature range of the detector should be broadened in order to use RGD for the analysis of heavier molecules. RGD therefore may, with further development, offer advantages over FID for selective development of ozone-precursor hydrocarbons in ambient air.

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