

Passive sampling and gas chromatographic determination of low concentrations of reactive hydrocarbons in ambient air with reduction gas detector

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ABSTRACT

The use of mercuric oxide reduction gas detection (RGD) for the passive sampling and capillary gas chromatographic determination of low concentrations of volatile organic compounds ($\leq C_6$) in ambient air is described. Sampling times are significantly reduced, compared with those required by the use of a flame ionization detector, due to the high sensitivity of RGD. The RGD signal due to the build-up of artifacts on polymeric sampling matrices during storage has also been investigated for Tenax-TA, Tenax-GR, Carbotrap and Chromosorb 106. The problem is at a minimum with Tenax-TA and GR, is more acute with Carbotrap, and is so severe with Chromosorb 106 that it prevents the use of this material for this application.

INTRODUCTION

Few volatile organic compounds (VOCs) are toxic in their own right at the concentrations found in the ambient atmosphere. Their main contribution to air pollution stems from their atmospheric reactions which lead to the formation of oxidizing species including peroxyacetyl nitrate (PAN), hydrogen peroxide and, especially, ozone [1]. Since the more reactive hydrocarbons (particularly the alkenes) have much higher potentials for tropospheric ozone formation than the non-reactive hydrocarbons (*e.g.*, alkanes) [2], the priority in atmospheric monitoring programmes which focus on photochemical ozone production is the speciation and quantitation of the reactive VOCs. Under some circumstances it would therefore be advantageous to utilize a detection system that has enhanced sensitivity towards alkenes but is rela-

tively insensitive to alkanes and other less reactive VOC species. This would result in a less complex chromatogram from an ambient air sample than is obtained with other universal detectors, for example the flame ionization detector, and so simplify peak identification.

Passive samplers were initially developed for the measurement of time-weighted average personal exposures to airborne contaminants in the workplace. Due to their many advantages over conventional pump samplers [3], passive samplers have also been employed for the monitoring of low concentrations [ppb (v/v) or ppt (v/v) mixing ratios] of organic vapours in ambient air in recent years [4,5]. However a major limitation of their use for this purpose is the increase in the blank signal due to the formation of artifacts on adsorbents during storage and exposure [6]. The long sampling periods necessitated by the very low sampling rates of passive samplers accentuates the problems of contamination and artifact formation. Although blank levels can be minimized by meticulous condition-

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ing of the adsorbing material, artifacts may build up on the unexposed matrix during storage. They may also build up during exposure of the sampler by reaction of ozone with the adsorbent [7], and this may raise detection limits to unacceptable levels. If the resultant blank signal is large relative to the analyte signal or is very variable, passive samplers will not be able to be used directly in rural air sampling. Therefore, sampling time should be as short as possible. This can be achieved by either designing a passive sampler with higher sampling rate or developing much more sensitive detection methods.

Reduction gas detection (RGD) was originally developed for detecting the reducing gases CO and H₂ [8]. It has also been used for the detection of acetaldehyde and acetone [9] and of isoprene (2-methyl-1,3-butadiene) [10]. The response of RGD to a variety of reactive hydrocarbons has been investigated using gas chromatography with packed columns [11]. It was shown that it is considerably more sensitive to alkenes than is flame ionization detection (FID), and has much greater sensitivity to alkenes than alkanes. RGD has also been developed successfully for the capillary gas chromatographic analysis of hydrocarbons up to C₆ with high resolution, but the peak shapes for compounds above C₆ (e.g., benzene, toluene etc.) are extremely broad and severely tailing [12].

Here, the use of RGD for the thermal desorption and capillary gas chromatographic determination of C₂–C₄ alkenes (qualitative) and C₅–C₆ alkenes (quantitative), including isoprene, in ambient air, using a passive sampling technique, is described, together with an assessment of the formation of artifacts on four different commonly used adsorbents.

EXPERIMENTAL

Principles of the reduction gas detector

The principle of operation of the reduction gas detector has been described elsewhere [11–13]. Briefly, it depends upon the reduction of solid mercuric oxide by a reducing gas X on a heated bed:



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.

Analytical system

Gas chromatographic measurements were made using a Hewlett-Packard 5890 Series II gas chromatograph fitted with a reduction gas detector (RGD-2, Trace Analytical, Menlo Park, CA, USA). The carrier gas used was helium. The capillary column used was a porous-layer open tubular (PLOT) (Al₂O₃/KCl) 50 m × 0.32 mm (Chrompack). A make-up gas line (stainless-steel tube, 1/8 in. I.D.; 1 in. = 2.54 cm) was used to supply helium to the detector to render it compatible with the capillary analytical column. A catalytic combustion filter was used in conjunction with an organic–water vapour trap (molecular sieve) for carrier gas purification. The flow-rate of make-up gas was 25 ml/min. An uncoated fused-silica capillary (15 cm × 0.53 mm) was used as the transfer line between the analytical column and the detector and was connected to the capillary GC column by a low dead-volume glass press-fit connector (Hewlett-Packard).

The exposed passive sampling tubes were thermally desorbed by a Chrompack Thermal Desorption Cold Trap (TCT) Injector, interfaced with the gas chromatograph, using helium carrier gas at a flow-rate through the tube of 35 ml/min. The desorbed analytes were retrapped by a deactivated fused-silica capillary trap (40 cm × 0.53 mm) [14] 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 capillary column in splitless mode. A schematic diagram of the whole TCT–GC–RGD system is shown in Fig. 1.

The GC system was calibrated using a Scotty (Chrompack) 15 ppm (v/v) mixed alkene calibration standard. This was injected into the carrier gas stream by means of a 1 ml gas-tight syringe via the TCT injector, and then carried by

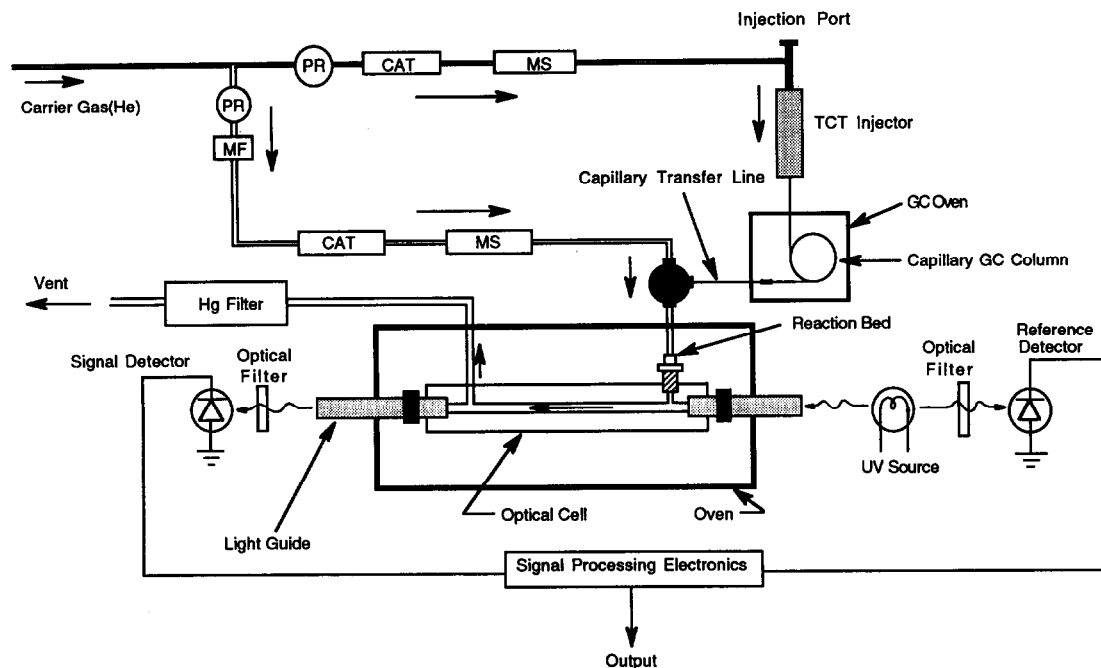


Fig. 1. Schematic diagram for TCT-capillary GC-RGD system. MS = Molecular sieve; CAT = catalytic combustion filter; MF = mass flow regulator; PR = pressure regulator.

helium gas through a heated empty Perkin-Elmer stainless-steel sampling tube to the capillary trap. Peak identification was by means of retention times with quantitation achieved using a VG Minichrom data handling system.

Adsorbents

Four commonly used adsorbents were investigated. Tenax-TA [size 60–80 mesh (284–328 μm), specific surface area 20 m^2/g , Chrompack] is a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide which has been widely used for air sampling. Carbotrap [20–40 mesh (402–568 μm), specific surface area 100 m^2/g , Supelco] is a graphitized carbon black. Tenax-GR (60–80 mesh, specific surface area 20–100 m^2/g , Chrompack) is a new adsorbent which consists of a Tenax matrix filled with 23% graphitized carbon. Its passive sampling performance has been investigated recently [6,15]. Chromosorb 106 (60–80 mesh, specific surface area 800 m^2/g , Chrompack) is a polyaromatic cross-linked resin which can be used for the sampling of more volatile compounds due to its high adsorption capacity.

The diffusion tubes were packed with 0.2 g

adsorbent (0.16 g for Tenax-TA), and conditioned for at least 16 h with helium flow at 35 ml/min at the following temperatures: 300°C (Tenax-TA), 320°C (Tenax-GR), 350°C (Carbotrap) and 250°C (Chromosorb 106). It should be mentioned that the low maximum operating temperature (250°C) of Chromosorb 106 necessitates the use of a conditioning time of at least 48 h. The optimum desorption conditions for these adsorbents have been investigated recently [16], and are 250°C for 5 min (Tenax-TA), 260°C for 6 min (Tenax-GR), 280°C for 8 min (Carbotrap), and 220°C for 10 min (Chromosorb 106).

Sampling procedures

Perkin-Elmer stainless-steel diffusion tubes (diameter 4.8 mm, diffusion length 15 mm for tubes with no diffusion cap) packed with different adsorbents were used for the sampling of volatile organic compounds in a rural area in the vicinity of Lancaster, north-west England, during February–March 1993. The relative humidity during sampling varied from 40 to 80%, and the temperature from 2 to 12°C. Swagelok caps were used to seal the conditioned sampling tubes prior

TABLE I
IDEAL UPTAKE RATES OF DIFFERENT HYDRO-CARBONS FOR PERKIN-ELMER DIFFUSION TUBE

Compounds	Uptake rates [ng/(ppm · min)]
1-Pentene	1.76
Isoprene	1.75
1-Hexene	1.87
Benzene	1.99

to sampling and during storage of exposed tubes prior to analysis. The passive sampling tubes were placed vertically with the open end downwards in a variety of outdoor locations and exposed for about 15 h. The concentrations of organic compounds in air were calculated using the following expression [3]:

$$\text{Analyte concentration (ppm)} = \frac{\text{mass uptake (ng)}}{\text{uptake rate [ng/(ppm · min)]} \times \text{exposure time (min)}} \quad (2)$$

The uptake rate in eqn. 2 was calculated using the following equation [3]

$$\text{Uptake rate [ng/(ppm/min)]} = \frac{DA}{L} \quad (3)$$

where D is the diffusion coefficient in air (cm^2/s), obtainable from the literature [17,18] or calculable for each analyte according to the Hirschfelder method (see ref. 18); A is the cross-sectional area of the diffusion tube ($=0.181 \text{ cm}^2$ for Perkin-Elmer diffusion tubes); and L is the diffusion length of the tube. The calculated uptake rates are shown in Table I.

RESULTS AND DISCUSSION

RGD signals resulting from system contamination and the formation of adsorbent artifacts

Passive sampling methods based upon adsorption onto a polymeric matrix and GC analytical systems are both susceptible to contamination problems, giving rise to unwanted detector signals. This was investigated with high-sensitivity

RGD by packing sampling tubes with different adsorbents, rigorously conditioning them as for field use and sealing with Swagelok caps. After storage for about 15 h they were thermally desorbed and analysed by the GC-RGD system as described above. The blank chromatograms before and after storage are shown in Figs. 2 and 3, respectively. The RGD response to impurities in the carrier gas and contamination of the TCT-GC system was also determined, and a typical chromatogram is shown in Fig. 2.

It can be seen from Fig. 2 that the high sensitivity of the RGD leads to large blank signals. The response due to system contamination is therefore much larger than that observed using conventional FID [14]. Tenax-TA, Tenax-GR and Carbotrap are seen to be very clean after conditioning, most of the blank signal being due to system contamination rather than being due to the adsorbants themselves, with the exception of the large, broad and tailing benzene peak at a retention time of 17 min. Although the latter part of the chromatogram for Chromosorb

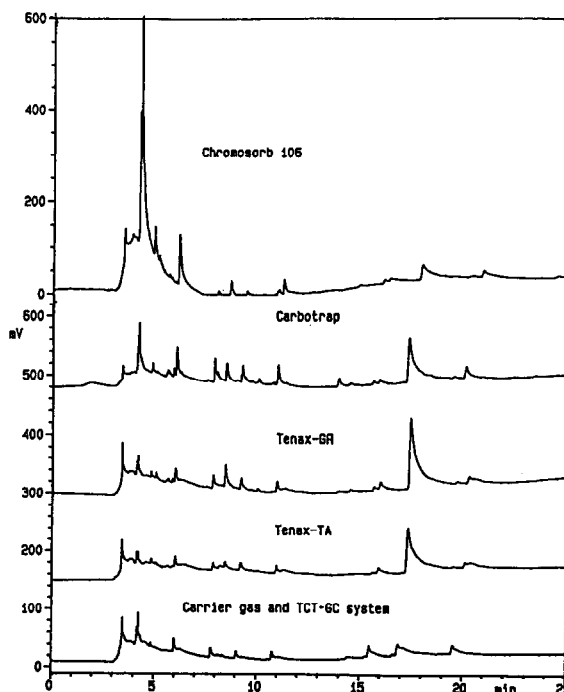


Fig. 2. Chromatograms of blank signals from RGD for different adsorbents before storage. GC conditions: 160°C (8 min) to 180°C at $3^\circ\text{C}/\text{min}$.

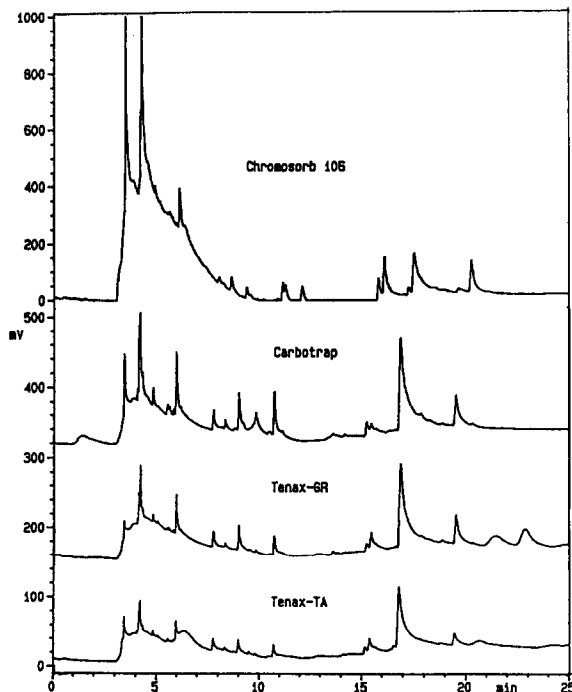


Fig. 3. Chromatograms of blank build-up signals from RGD for different adsorbents after storage for about 15 h. GC conditions: 160°C (8 min) to 180°C at 3°C/min.

106 is relatively clean, there is considerable noise between retention times of 3 and 7 min, and this adsorbent may therefore not be suitable for the sampling and analysis of compounds (C_1 - C_4) which elute in this range.

Fig. 3 shows the chromatograms resulting from different adsorbents after storage for 15 h. All four adsorbents showed increased levels of contamination to different extents, with Tenax-TA producing the least noisy signal and Chromosorb 106 (especially in the initial part of the chromatogram) the most. It is unlikely these peaks represent contaminants from ambient air, adsorbed during storage, since the tubes were sealed tightly with Swagelok caps [6]. Rather it seems likely they represent compounds generated within the adsorbents themselves during storage, possibly by degradation of the polymers and low-molecular-weight polymers (by-products) and impurities in the technical-grade reagents used for polymer production, or oxidation of the polymers and the by-products by the residual reactive inorganic gases (e.g., ozone) within the

tube. This is less likely since the tubes were purged with helium at high temperatures for 16 h. Such artifact formation processes may be unavoidable, and reduction of the sampling and storage periods to the minimum practicable may be the only way to minimize the problem.

Passive sampling of VOCs in ambient air

Fig. 4 shows representative chromatograms of samples collected with different adsorbents by exposure for about 15 h to ambient air at the same site. The scale differences of the chromatograms should be taken into account when comparing Figs. 2 and 3 with Fig. 4. The amounts of analytes adsorbed onto Tenax-TA are relatively small, compared with the blank build-up signal (shown in Fig. 3), due to the weak adsorption affinity of Tenax-TA for the light hydrocarbons ($\leq C_6$). For Tenax-GR and Carbotrap, the amounts of compounds adsorbed onto the adsor-

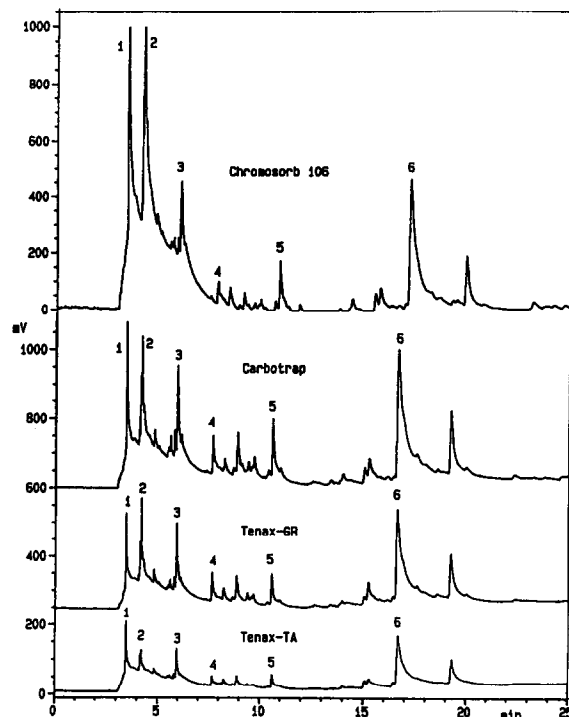


Fig. 4. Chromatograms of passive sampling of VOCs in ambient air for about 15 h for different adsorbents from RGD. GC conditions: 160°C (8 min) to 180°C at 3°C/min. Peaks: 1 = propylene; 2 = 1-butene; 3 = 1-pentene; 4 = isoprene; 5 = 1-hexene; 6 = benzene.

bents are significant compared with their corresponding blank build-up values. In the case of Chromosorb 106, the amounts of most compounds adsorbed are similar to their blank build-up values. Chromosorb 106 and Tenax-TA may therefore not be suitable for this purpose. The other disadvantage of using Chromosorb 106 is that its thermal desorption gives rise to significant amounts of higher-molecular-weight compounds ($\geq C_{10}$) on the GC column to which RGD is sensitive and which must then be removed by lengthy column conditioning.

Because the passive sampling technique may not be suitable for the sampling of very light hydrocarbons ($C \leq 3$) due to their extremely high volatility [19], and the trapping efficiency of the TCT capillary cold trap for very light hydrocarbons ($C \leq 4$) decreases significantly with increasing carrier gas flow-rate [14], propylene and 1-butene were not quantified although they are clearly identifiable in the chromatogram. The concentrations of 1-pentene, isoprene, 1-hexene and benzene in ambient air samples collected on Tenax-GR and Carbotrap were calculated by subtracting their corresponding blank signals using eqn. 2 above. The results are summarized in Table II.

It can be seen from Table II that the concentrations of the four selected hydrocarbons vary from as low as 0.03 ppb for isoprene to as high as 1.0 ppb for benzene in the 17 samples collected at this site. The sources of the olefins and benzene in rural air will include vehicle exhaust

TABLE II
TYPICAL CONCENTRATIONS OF SELECTED POLLUTANTS IN AMBIENT AIR IN NORTH-WEST ENGLAND

Compounds	Concentrations (ppb)		
	n^a	Range	Mean
1-Pentene	18	0.06–0.28	0.16
Isoprene	17	0.03–0.19	0.08
1-Hexene	18	0.04–0.19	0.09
Benzene	17	0.15–1.0	0.41

^a n = Number of samples.

emissions, fuel leakage and evaporation, solvent evaporation and industrial emissions, with resultant concentrations lower than those observed in urban source areas. Isoprene is the predominant hydrocarbon emitted by a number of deciduous trees and other plant species [20] but its low concentrations may be attributed to the low density of trees in north-west England and to the lack of photosynthetic activity, low temperatures and light intensities prevailing during the sampling periods.

Comparisons between the chromatograms from RGD with those from FID

Fig. 5 shows the typical GC-FID chromatograms obtained from passive sampling of VOCs in ambient air for Carbotrap and from its blank build-up. Compared with the RGD chromatograms shown in Fig. 4, it can be seen clearly that the chromatograms from RGD looks more simple than those from FID due to the high selectivity of RGD, and many alkanes detected by FID have no or extremely low responses in RGD. Because of the high sensitivity of RGD, the corresponding peaks from the RGD chromatograms are much higher than those from the FID chromatogram, even though the sampling

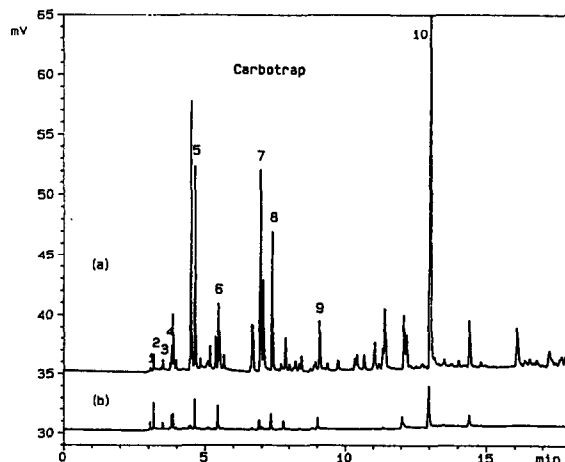


Fig. 5. (a) Chromatogram of passive sampling of VOCs in ambient air for about 4 days for Carbotrap from GC-FID; (b) chromatogram of Carbotrap blank build-up for about 4 days from FID. GC conditions: 160°C (5 min) to 200°C at 5°C/min. Peaks: 1 = propane; 2 = propene; 3 = *n*-butane; 4 = 1-butene; 5 = *n*-pentane; 6 = 1-pentene; 7 = isoprene; 8 = *n*-hexane; 9 = 1-hexene; 10 = benzene.

time for FID is about 8 times longer than for RGD. The present version of RGD was originally designed for use with packed GC columns, not capillary columns, and therefore the peak resolution from RGD is not optimum. This may be improved significantly by designing a micro-RGD system with minimum dead volume.

CONCLUSIONS

RGD is highly sensitive and selective for the analysis of reactive hydrocarbons. Here, its use for the determination of four selected VOCs in rural ambient air, using passive sampling, thermal desorption and capillary GC separation has been demonstrated. Sampling times were significantly reduced compared with those necessary with FID, due to the high sensitivity of the detector. Further development of the use of this detector for capillary GC environmental analysis is certainly warranted.

The RGD responses to the blank signals resulting from the use of four adsorbents (Tenax-TA, Tenax-GR, Carbotrap and Chromosorb 106) have also been investigated. The problem is at a minimum with Tenax-TA and GR, is more acute with Carbotrap, and is so severe with Chromosorb 106 that it prevents the use of this material for this application.

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