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# A Comparison of Photoionisation Detection Gas Chromatography with a Tenax GC Sampling Tube Procedure for the Measurement of Aromatic Hydrocarbons in Ambient Air

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Photoionisation detector/gas chromatography (PID/GC) provides an opportunity for direct measurement of aromatic hydrocarbons in ambient air at ppb levels without preconcentration. The use of a portable PID/GC instrument has been evaluated and compared with a Tenax GC sampling tube method. The minimum detectable concentration using PID/GC was determined to be 0.3 ppb for benzene and toluene and 1.0 ppb for C8-alkylbenzenes. At high concentrations (<100 ppm), linearity of detector response was maintained by reduction in sample injection volume. In addition, due to the specificity of the detector, the instrument was found to be suitable for the measurement of aromatic hydrocarbons in vehicle exhaust by direct injection without interference from water vapour. Significant difficulties in quantitative sampling of concentrations typical of industrial atmospheres (>1 ppm), were found using the Tenax GC preconcentration method. On-site measurement of aromatic hydrocarbons at a busy urban road-side location was undertaken using the two techniques. Measured concentrations of benzene and toluene compared favourably although the PID/GC technique was found to be inconsistent in the detection of low ambient concentrations of higher alkylbenzenes. However it is evident that rapid and direct measurement of a wide range of concentrations can be achieved using the PID/GC techniques which complement and in some cases supercede existing preconcentration techniques.

**KEY WORDS:** Photoionisation detector/gas chromatography (PID/GC), aromatic hydrocarbons, Tenax GC sampling method.

## INTRODUCTION

Aromatic hydrocarbons account for approximately 30% (by weight) of the total hydrocarbons in the atmosphere (excluding C<sub>2</sub> hydrocarbons).<sup>1,2</sup> The dominant sources of these compounds are motor vehicle evaporative and exhaust emissions and losses resulting from the use of solvents in industrial applications. Benzene has received a great deal of attention because of its carcinogenic potential.<sup>3</sup> Toluene and other alkylbenzenes are also suspect carcinogens, although detailed toxicity studies are not yet complete. Few data exist on possible health effects of these compounds resulting from long term exposure to low concentrations although this is an area of increasing concern.<sup>4,5</sup>

Measurements of these compounds in ambient air and in the workplace have generally involved preconcentration on solid adsorbents, the most popular of which is Tenax GC.<sup>6,7</sup> Analysis of the sampling tubes is frequently achieved by thermal desorption/gas chromatography utilising flame ionisation detection (FID)<sup>8,9</sup> or by gas chromatography/mass spectrometry (GC/MS).<sup>10,11</sup> The development of the photoionisation detector (PID) for gas chromatography provides a method of direct measurement of ambient air for specific volatile organics without preconcentration.<sup>12-15</sup> Recent publications have described PID/GC techniques for measurement of chlorobenzenes,<sup>15</sup> mercaptans,<sup>16</sup> formaldehyde,<sup>17</sup> ethylene oxide and ethylene dibromide<sup>18</sup> in ambient air. The PID provides high sensitivity for the measurement of aromatic hydrocarbons in air and an evaluation of its use in comparison to a Tenax GC sampling tube method<sup>9</sup> is described.

## EXPERIMENTAL

Standard atmospheres of various concentrations (0–100 ppm) of benzene, toluene, *o*-, *m*- and *p*-xylene and ethylbenzene were established in glass flasks by static dilution of headspace vapour of the pure compounds. Sample air from the glass flasks was directly injected by means of gas-tight syringes (0.01–1 ml) into a Photovac Model 10A10 portable PID/GC (Photovac, Thornton, Ontario, Canada). The PID/GC was fitted with a Teflon column

(1.5 m × 3.1 mm o.d.) packed with 5% SE 30 on Chromosorb G 100/120 (Chrompack, London, U.K.). Hydrocarbon-free air (Air Products, Bracknell, U.K.) was used as carrier gas at a flow-rate of 15 ml min<sup>-1</sup>. The instrument was operated at ambient temperature. Chromatographic traces were recorded on a strip-chart recorder. The detection limits for individual compounds were defined as 2.5 times the signal to noise ratio.

Exponential dilution of the flasks with clean air provided a secondary method of producing standard atmospheres and provided a method of comparison with the Tenax GC sampling tube method.

A constant-flow pump (Du-Port, Stevenage, U.K.) was used to draw clean air (activated charcoal filtered ambient air) through the flask and onto stainless steel sampling tubes (74 × 4 mm i.d. packed with Tenax GC (0.13 g, 35/60 mesh, Chrompack, London, U.K.) for known periods of time. The concentration of organic vapour decayed in the flask according to the equation

$$C = C_0 e^{-Ft/V} \quad (1)$$

where  $C$  = the concentration at time  $t$  (min)

$C_0$  = the initial concentration

$F$  = dilution flow-rate (ml min<sup>-1</sup>)

$V$  = volume of the dilution flask

Sampling tubes were thermally desorbed at 250°C in a Bendix flasher unit (Bendex, Milton Keynes, U.K.) interfaced with a Hewlett Packard 5700 A GC/FID (Hewlett Packard, Winnersh, U.K.). The GC was fitted with a stainless steel column (2 m × 3.1 mm o.d.) packed with 10% TCEP on Chromosorb P HP, 100–120 mesh (Phase Separations, Queensferry, U.K.) operated isothermally at 70°C with a carrier gas flow of 40 ml min<sup>-1</sup> oxygen-free nitrogen. The FID temperature was 250°C. The Tenax GC sampling tube procedure has been previously evaluated for the measurement of aromatic hydrocarbons in ambient air.<sup>9</sup>

On-site measurement of ambient air utilising the PID/GC took place in conjunction with a previously reported survey of aromatic hydrocarbons utilising the Tenax GC sampling tube procedure<sup>19</sup> at a road-side urban location (Exhibition Road, London, SW7). Ambient air sampling took place over 20 min periods at a flow-rate of 100 ml min<sup>-1</sup> using the sampling tube method. Direct

measurement of ambient air utilising the PID/GC was also performed every 20 min.

The PID/GC was also used for the measurement of aromatic hydrocarbons in motor vehicle exhaust during dynamometer ECE-15<sup>23</sup> and 90 km h<sup>-1</sup> constant speed tests while operating on various test fuels of varying aromatic and alkyl lead content. The test car exhaust was diluted by a constant volume sampling system and then collected in a preconditioned Tedlar bag (1580 × 832 mm). Aliquots were then taken from the bag, *via* a septum capped sampling point and injected into the PID/GC fitted with a 2 m × 3.1 mm o.d. Teflon column packed with 1.5% OV17+1.95% QF1 on Supelcoport 100/120.

## RESULTS AND DISCUSSION

Minimum detection limits for benzene, toluene and C8 alkylbenzenes are presented in Table I. The PID is most sensitive for benzene and is able to detect 0.8 pg in a 1 ml sample (maximum injection volume of this instrument). The detection limits compare well with other published data (e.g. 0.6 pg benzene) utilising PID/GC.<sup>2</sup> A typical concentration/response graph for benzene is presented in Figure 1. Using 1 ml sample aliquots, calibrations above 1 ppm benzene, 3 ppm toluene and 4 ppm C8 alkylbenzenes became non-linear. Because of the high sensitivity of the instrument, however, it was possible to reduce injection volumes to 0.01 ml and thus maintain linearity over a wide concentration range as demonstrated in Figure 2.

TABLE I  
Minimum detection limits of aromatic hydrocarbons in air by PID/GC

Compound	Minimum concentration ppb	Detection limit pg <sup>a</sup>
benzene	0.25	0.8
toluene	0.32	1.2
ethylbenzene	0.94	4.2
<i>o</i> -xylene	0.94	4.2
<i>m</i> -xylene	0.97	4.3
<i>p</i> -xylene	0.97	4.3

<sup>a</sup>1 ml sample aliquot.

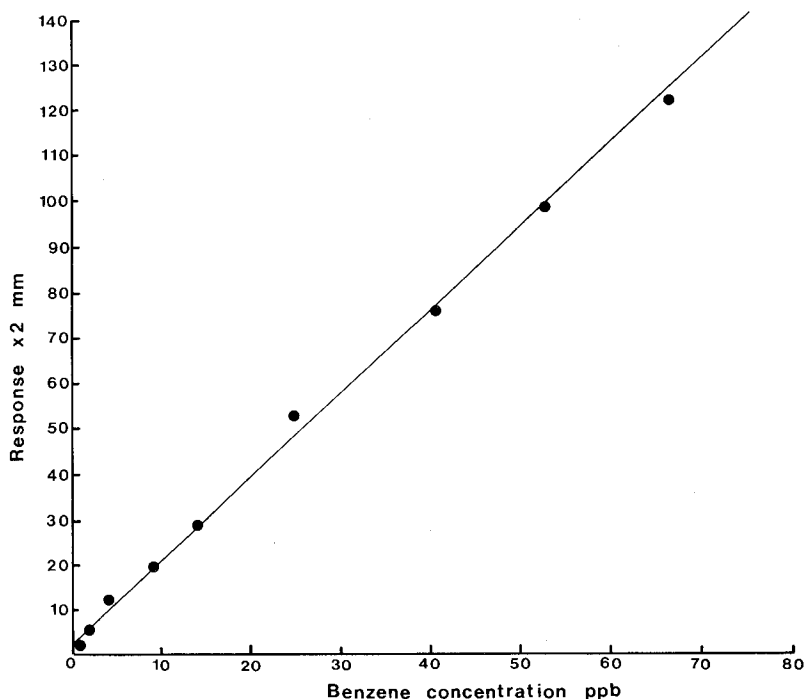


FIGURE 1 PID response to ambient air concentrations of benzene.

The method of exponential dilution has been used previously to introduce known amounts of organic vapour onto Tenax GC sampling tubes for calibration purposes.<sup>9</sup> The results of introducing high concentrations of benzene and toluene onto Tenax GC sampling tubes are presented in Figure 3 and are compared with the FID response to direct injections of the same mass. This demonstrates that at high concentrations the efficiency of sampling is less than at low concentrations and that an arbitrary limit for the linearity of adsorption of these compounds was achieved at approximately 1 ppm.

This is in direct agreement with the work of Vejrosta *et al.*,<sup>20</sup> determining distribution constants of benzene on Tenax GC at various gas phase concentrations by direct measurements of sorption equilibria and which concluded that the retention volume was independent of benzene concentration on Tenax GC only up to a concentration of *ca* 1 ppm.

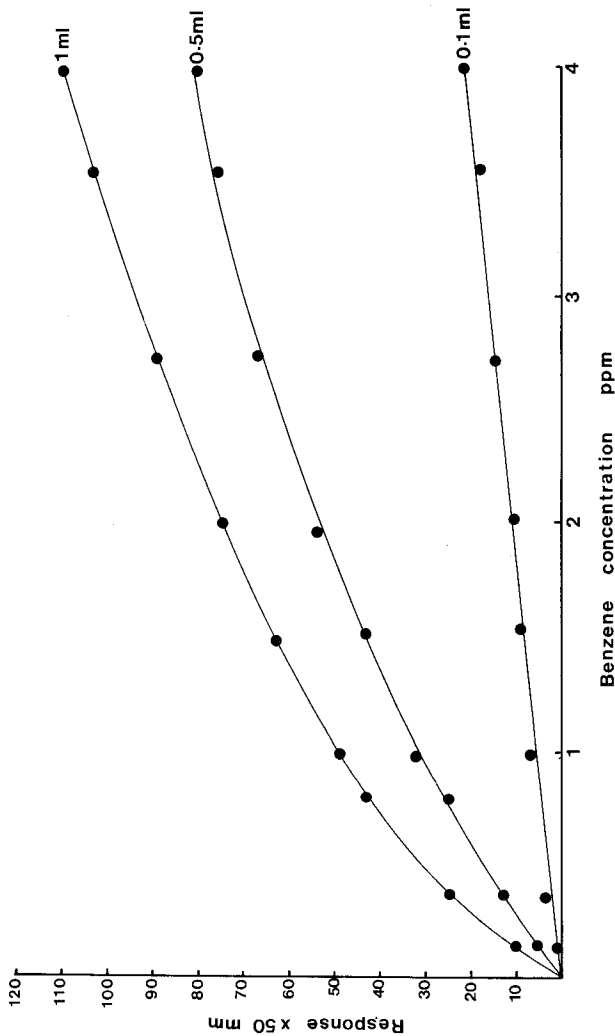


FIGURE 2 Effect of sample injection volume on linearity of PID response.

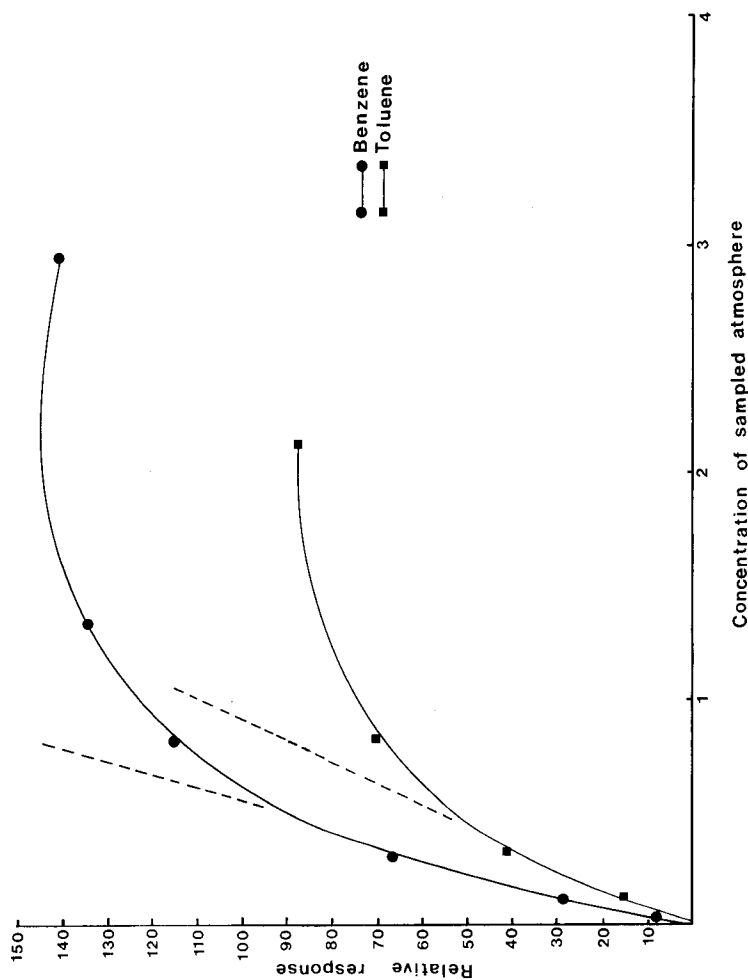


FIGURE 3 Effect of introducing high concentrations of benzene and toluene onto Tenax GC sampling tubes as compared to the FID response to direct injections of equivalent mass (indicated by the dashed line).



It is evident therefore that the sampling tube method is not suitable for quantitative measurements of high concentrations ( $>1$  ppm) of aromatic hydrocarbons in air which may occur in the workplace. The threshold limit value for benzene is 10 ppm (8 h weighted average)<sup>21</sup> and when concentrations in this range are encountered, the PID/GC is more suitable for ambient air measurement than the Tenax GC sampling tube procedure.

Close agreement between measured concentrations of benzene and toluene was found throughout the on-site monitoring period as demonstrated by data presented in Table II. The mean concentration of benzene (10.6 ppb), determined by the PID/GC method was 20% higher than that determined by the sampling tube method, well within the variability (arithmetic mean/standard deviation  $\times 100$ ) of the method. Similarly PID/GC measurements of toluene were 10% lower than those determined by the sampling tube method. However, concentrations of ethylbenzene, *o*-, *m*- and *p*-xylene were too low to be determined consistently by the PID/GC method.

These findings are in accord with a previously reported automated PID/GC technique which was used successfully to measure benzene and alkylbenzenes in California.<sup>22</sup> It must be noted that the Tenax GC sampling tube procedure was able to measure ethylbenzene (0.9

TABLE II  
Comparison of measurements of ambient concentrations of benzene and toluene by PID/GC and Tenax GC sampling tube techniques

Compound	Concentration (ppb)	
	PID	Tenax GC
Benzene $\bar{x}$	10.6	8.8
$\sigma$	5.4	3.6
min	0.9	1.0
max	23.0	21.4
<i>n</i>	93	109
Toluene $\bar{x}$	12.1	13.5
$\sigma$	8.3	7.7
min	1.0	1.0
max	40.0	38.0
<i>n</i>	93	109

$\pm 0.6$  ppb), *m*- and *p*-xylene ( $2.8 \pm 1.1$  ppb) and *o*-xylene ( $1.23 \pm 0.5$  ppb) at the urban site which were similar to other reported values.<sup>19</sup>

The two methods provide two distinct types of information on aromatic hydrocarbon concentrations. Instantaneous concentrations are measured by the PID/GC using essentially a "grab" sampling method whereas the adsorbent tube method provides information on the average concentration over the sampling period. This is reflected in the greater variability of benzene and toluene measurements (Table II) and is further demonstrated in Figure 4 where a typical variation of toluene concentrations with time of day is presented.

Direct measurements of aromatic hydrocarbons by PID/GC is less complex than the Tenax GC sampling tube method which involves collection of sample, thermal desorption and subsequent analysis by GC/FID. The PID/GC method is also amenable to automation by the use of gas sampling valves as described in the work of Hester and Meyer.<sup>22</sup>

The PID/GC instrument was capable of measuring from sub-ppb to 100 ppm concentrations of aromatic hydrocarbons. Owing to the specificity of the detector, the instrument was also suitable for the measurement of vehicle exhaust emissions of aromatic hydrocarbons by direct injection. An example of a typical exhaust chromatogram is presented in Figure 5 and the results of a series of dynamometer studies have been used to demonstrate the influence of fuel composition and driving conditions on exhaust emissions of aromatic hydrocarbons.<sup>23</sup>

## CONCLUSIONS

The PID/GC method offers high sensitivity for the measurement of aromatic hydrocarbon in air. The minimum detectable concentration was determined as 0.3 ppb for benzene and toluene and 1.0 ppb for C8-alkyl benzenes. The PID/GC is capable of measuring a wide range of aromatic hydrocarbon concentrations (ppb to 100 ppm) and has the advantage of ease of measurement as compared to the Tenax GC sampling method. In addition the Tenax GC sampling tube method has been demonstrated to have significant limitations when sampling concentrations above 1 ppm.

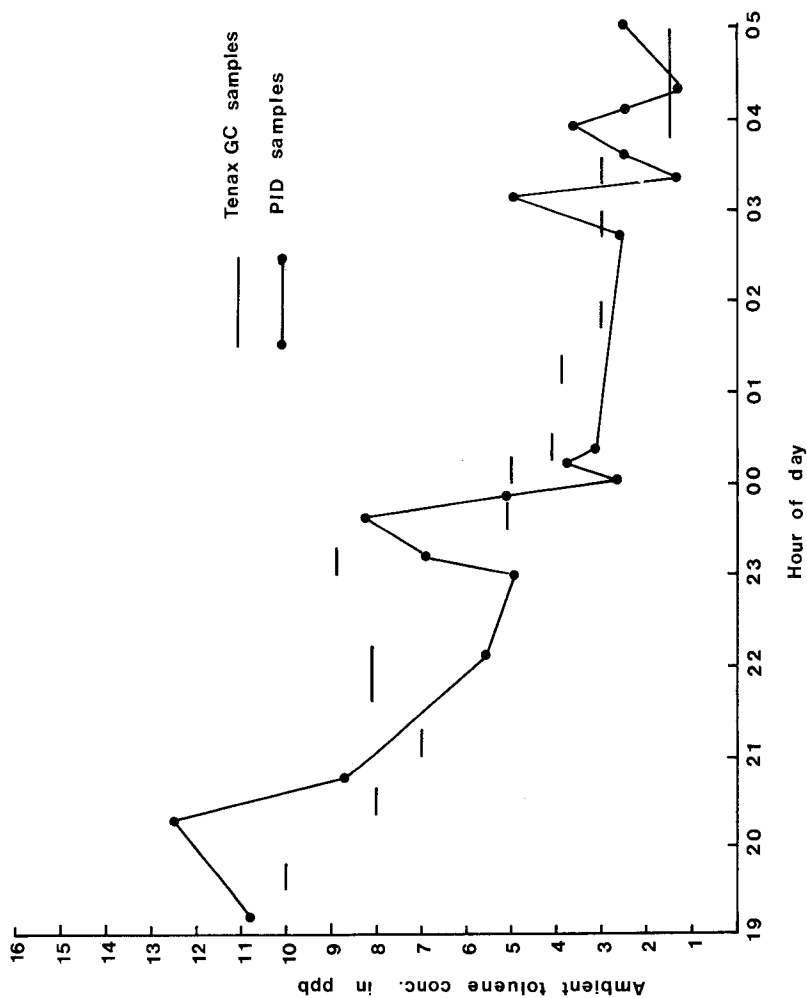


FIGURE 4 Example of typical variations of concentrations of toluene with time of day as determined by PID/GC and the Tenax GC sampling tube procedure.

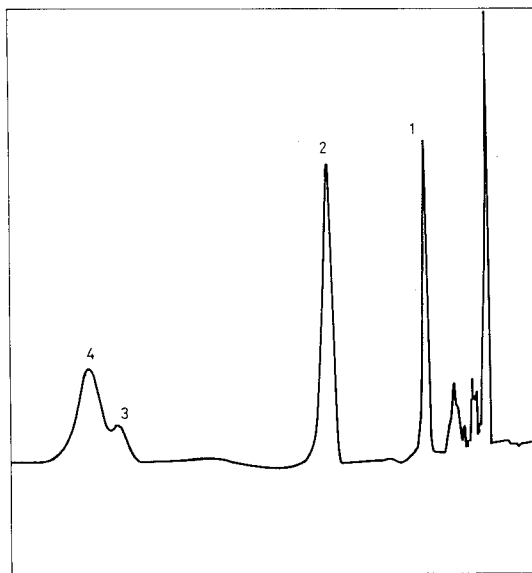


FIGURE 5 Example of a vehicle exhaust sample. Carrier gas flow-rate =  $20 \text{ ml min}^{-1}$ , attenuation 100, chart speed =  $10 \text{ mm min}^{-1}$ . 1 = benzene, 2 = toluene, 3 = ethyl benzene, 4 = *m*- and *p*-xylene.

Field studies have shown that ambient concentrations measured by the PID/GC at a busy road-side urban location were in the range  $10.6 \pm 5.4 \text{ ppb}$  for benzene and  $1.21 \pm 8.3 \text{ ppb}$  for toluene which compared well with concentrations determined by the Tenax GC sampling tube method. Concentrations of C8-alkylbenzenes were too low to measure consistently using the PID/GC technique although the Tenax GC sampling tube method was able to achieve this.

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