Benzene and toluene profiles in ambient air of Delhi as determined by active sampling and GC analysis

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Present study aims to standardise methodology for the measurement of benzene and toluene using active sampling onto sorbent tubes and to investigate their existing profile in the urban environment of Delhi, India. Samples were collected by active sampling onto preconditioned stainless steel standard adsorbent tubes packed with Tenax TA adsorbent using a portable constant low flow volume sampler. Sampling flow rate ranged 20-25 ml min\(^{-1}\) and sampling duration 1.30-2.30 h. Samples were analysed by thermal desorption followed by gas chromatography coupled with automated thermal desorber. The desorption system was provided with a cryogenic trap filled with Tenax TA adsorbent. External calibration was performed using five concentration levels of standards solutions in carbon disulfide (CS\(_2\)). Linear fit in all cases were found good with R\(^2\) > 0.99. Benzene concentration ranged 33.69-174.62 µg m\(^{-3}\) whereas toluene ranged 45.18-228.83µg m\(^{-3}\) in the vicinity of petrol pump along with heavy traffic roadside at Preet Vihar location. Average benzene and toluene concentration of ambient air at ITO (near a busy traffic intersection) ranged 13.03-33.06 µg m\(^{-3}\) and 19.71-57.64 µg m\(^{-3}\) respectively. While at East Arjun Nagar (a residential cum institutional area), levels were 17.69 µg m\(^{-3}\) and 22.81 µg m\(^{-3}\) for benzene and toluene, respectively. Present study indicated that the concentration of benzene at all the sites was higher than the limit values prescribed in the UK (16 µg m\(^{-3}\), running annual average) and European Commission (5 µg m\(^{-3}\), annual average). Average toluene and benzene ratio ranged between 1.29 µg m\(^{-3}\) in residential cum institutional area to 1.74 µg m\(^{-3}\) at busy traffic intersection.

Keywords: Active sampling, Benzene, Toluene, Toxic air pollutants, Volatile organic compounds (VOCs)

Introduction

In the industrial countries, traffic accounts for emission\(^1\) (> 70 %) of volatile non-methane hydrocarbons (NMHCs) in the atmosphere. The composition of NMHCs is quite different in various cities, but the predominant species are alkanes and aromatic hydrocarbons (AHs), majority of which are toxic and produce toxic intermediates in photochemical reaction. Since 1980, a variety of studies have documented toxic air emissions from mobile sources as a major contributor to overall health risk\(^2\). These compounds also play a key role in the formation of secondary atmospheric pollutants, particularly ozone\(^3\)-\(^4\).

The U.S. Clean Air Act Amendments (1990) specifically targeted reductions in 5 toxic air pollutants (benzene, 1,3-butadiene, formaldehyde, acetaldehyde and polycyclic AHs) from mobile sources. Many urban centers have been studied for levels of these pollutants, and their possible sources and impacts\(^4\)-\(^8\). Benzene, present in both exhaust and evaporative emissions from vehicles, is a liquid at normal ambient temperature, but readily evaporates and small amounts are detected in the atmosphere. Almost all the benzene found at ground level in the northern hemisphere is likely to have resulted from human activities, particularly the combustion of petroleum fuel by motor vehicle engines and also cigarette smoking\(^9\).

In atmosphere, transport sector\(^10\) releases benzene (80-85%) as follows: vehicular, 80-90; evaporation, 10-20; and transportation, delivery and distribution at petrol station, 3-6%. Volatile organic compounds (VOCs) constitute one group of pollutants known for their toxicity to some species (benzene) and for their major role in photo-oxidation and formation of ozone and peroxyacetyl nitrates. VOCs have direct toxic effects from carcinogenesis to neurotoxicity\(^4\),\(^11\) on humans and animals above certain dose. Other adverse health effects of benzene are respiratory disorder, narcosis, change in blood pattern, anaemia and leukaemia. Toluene is less toxic and causes drowsiness, impaired co-ordination, and liver and kidney damage\(^12\)-\(^15\) than benzene.

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The present study investigates existing levels of VOCs in ambient air along with standardization of methodology for the measurement of benzene and toluene using active sampling onto sorbent tubes.

**Experimental Details**

**Sampling Site**

Delhi is positioned with the Thar Desert of Rajasthan to the west and southwest, central hot plains to the south and Gangetic plains of Uttar Pradesh to the east while cooler hilly regions to the north. It is situated at latitude 28° 24' 17" and 28° 53' 00" (North); longitude 76° 45' 30" and 77° 21' 30" (East) at about 160 km south of Himalayas at an elevation of 216 m above the mean sea level. Delhi is drained by river Yamuna. Monthly mean normal temperature ranges from 14.3°C in January (min. 2-3°C) to 34.5°C in June (max. 45°C). The annual mean temperature is 25.3°C. Delhi region experiences total annual rainfall of 700-800 mm; maximum during monsoon months (max. in July, > 200mm). Sampling locations (Fig. 1) were as follows:

**ITO (Bahadurshah Zafar Marg)**

ITO is one of the busiest stretch on a main road connecting New Delhi with Old Delhi. During peak office hours, traffic management becomes extremely difficult with long waits at the traffic signals. Two thermal power plants located in the nearby area of ITO could also have impact on air quality of this area.

**Preet Vihar (Vikas Marg)**

This sampling site was selected in the vicinity of petrol pump. It is situated in the eastern part of Delhi and has one of the busiest petrol pumps along with heavy traffic roadside.

**East Arjun Nagar**

This site is situated in the East of Delhi about 2 km from the National highway. This location is a flat plateau with residential, institutional and newly developing commercial area.

**Sampling**

Samples (length 9 cm, internal diam 0.5 cm) were collected by active sampling onto stainless steel adsorbent tubes (standard Perkin-Elmer sampling tubes, Part no. M041-3595) and were packed with Tenax TA adsorbent (250 mg and surface area = 35 m²g⁻¹). Air samples were drawn through the tubes using a portable low flow and constant volume
sampler (SKC-make). The sampling flow rate ranged 20-25 ml min\(^{-1}\) and sampling duration 90-150 min. The sampling pump was calibrated by a flow meter (SKC make electronic digital flow calibrator) before and after collection of each sample batch. The average of these two flow rates was used as the sample flow rate in all concentration calculations. In this study, final rate did not shift more than 5 percent from the initial values. Before using in the field, sample tubes were conditioned at 250°C and 300°C for 2 h, respectively, and then checked if there was any contamination left (blank run). Blank levels were also estimated by analysis of tubes brought to the sampling site but not used.

**Protection and Storage of Samples**

As the pump was turned off, tubes were removed from sampling train and two open sides were tightly closed using swagelok fittings and PTFE ferrule to avoid any desorption and contamination. Tubes were wrapped with Al-foil and placed in an opaque, clean and airtight container, which was immediately sent wrapped with Al-foil and placed in an opaque, clean and airtight container, which was immediately sent back to laboratory and placed in a refrigerator (< 4°C).

**Analysis**

Samples were analyzed by thermal desorption followed by gas chromatography\(^{1,16-19}\). Gas chromatograph (Turbomatrix XL, Perkin Elmer) was coupled with Automated Thermal Desorber (ATD – 400, Perkin Elmer). The desorption system was provided with a cryogenic trap filled with Tenax TA adsorbent. This trap was cooled to ~30°C with peltier elements. Desorption parameters are as follows: Purge time, 1 min (after leak test air is purged to reduce analyte oxidation); Tube oven temp., 300°C (desorb time, 12 min); Cold trap low temp., -30°C; Heat rate of cold trap, 40°C sec\(^{-1}\) up to 225°C for 20 min; Heated valve temp. (6 Port rotary valve), 225°C; Transfer line temp., 225°C; Inlet & outlet split, 50 & 20 ml min\(^{-1}\) respectively before and after cold trap; and Carrier gas, \(N_2\) at 24 psi. Gas chromatographic (GC) parameters are as follows: Column—Capillary, PE-5, 25 m x 200μm, df = 0.33μm; Detector, Flame Ionization Detector (FID) at 250°C; Air & \(H_2\) gas, 400 ml min\(^{-1}\) & 40 ml min\(^{-1}\) (10:1); Carrier gas, \(N_2\) (1 ml min\(^{-1}\)); Attenuation & range, -6 & 1; Oven, Initial temp.: 50°C hold for 2 min, Ramp1: 8.0°C min\(^{-1}\) to 140°C hold for 3 min, Ramp2: 10.0°C min\(^{-1}\) to 250°C hold for 3 min; and Retention time for benzene and toluene, 3.22 and 4.54 min, respectively.

Chromatographic grade pure hydrogen and air were used for the FID flame, while pure \(N_2\) was used as a carrier gas. The GC set up was connected to a computer to store and evaluate the output data. Each target compound was identified by its retention time to those obtained for the calibration standards under specified chromatographic conditions and quantification was accomplished by using multipoint external standard curves.

**Calibration of Instrument**

External calibration was performed using various concentrations of standard solutions in CS\(_2\). Liquid phase calibration standards were prepared by using known volume of chromatographic grade pure benzene and toluene into vials and diluting with CS\(_2\) (all the substances were provided by Merck). The concentration of analytes in the calibration solution was measured using their densities. Five levels of calibration standards (0.0435, 0.087, 0.174, 0.261 and 0.348μg μl\(^{-1}\) standard solution) were used to prepare the calibration curves.

Liquid standards were introduced onto the conditioned sorbent tube using a conventional GC syringe. Linear fit in all cases was found good, with regression coefficient (\(R^2\)) > 0.99. Each time, before sample analysis, calibration curve was confirmed by analysing a mid range standard solution. If the percentage difference in response factor was more than 15 percent, GC was recalibrated. The solvent used for standards (CS\(_2\)) was analysed to check if there was any contamination present. There was no contamination found in CS\(_2\) for making standard solution.

**Results and Discussion**

The concentrations of benzene and toluene varied with the peak and lean period of the day (Tables 1-3). In most cases, concentration was found higher in the morning time, followed by a drop during noon period and further increase in the evening rush hours. However, on June 18, 2002 (ITO location) and June 27, 2002 (Preet Vihar location), their concentrations were found higher during noon period. This is because traffic density on these routes remains high throughout the day and traffic volume changes on the selected routes between the two periods was small. Benzene and toluene do not dissipate into the environment immediately after release. Benzene and toluene as mono-aromatic hydrocarbons react only very slowly with \(O_3\) and \(NO_3\) radicals, their rate
TABLE 1—Concentrations of benzene and toluene with toluene to benzene ratio monitored at peak and lean periods of the day in the vicinity of petrol pump, Preet Vihar, Delhi

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Duration</th>
<th>(C_{\text{benzene}}) (\mu\text{g m}^{-3})</th>
<th>(C_{\text{toluene}}) (\mu\text{g m}^{-3})</th>
<th>(C_{\text{toluene}}/C_{\text{benzene}})</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 May, 2002</td>
<td>MPP</td>
<td>39.50</td>
<td>58.53</td>
<td>1.23</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>NLP</td>
<td>34.92</td>
<td>41.08</td>
<td>1.18</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>EPP</td>
<td>26.64</td>
<td>35.94</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>33.69</td>
<td>45.18</td>
<td>1.34</td>
<td>1.34</td>
</tr>
<tr>
<td>19 June, 2002</td>
<td>MPP</td>
<td>188.25</td>
<td>253.14</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>NLP</td>
<td>145.07</td>
<td>180.23</td>
<td>1.24</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>EPP</td>
<td>190.53</td>
<td>253.06</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>174.62</td>
<td>228.83</td>
<td>1.31</td>
<td>1.31</td>
</tr>
<tr>
<td>27 June, 2002</td>
<td>MPP</td>
<td>68.75</td>
<td>114.50</td>
<td>1.65</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>NLP</td>
<td>112.14</td>
<td>174.67</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>EPP</td>
<td>139.49</td>
<td>187.67</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>106.79</td>
<td>158.95</td>
<td>1.49</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Note: MPP, Morning peak period; NLP, Noon lean period; EPP, Evening peak period

TABLE 2—Concentrations of benzene and toluene with toluene to benzene ratio monitored at peak and lean periods of the day at ITO (Bahadurshah Zafar Marg), Delhi

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Duration</th>
<th>(C_{\text{benzene}}) (\mu\text{g m}^{-3})</th>
<th>(C_{\text{toluene}}) (\mu\text{g m}^{-3})</th>
<th>(C_{\text{toluene}}/C_{\text{benzene}})</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 April, 2002</td>
<td>MPP</td>
<td>37.67</td>
<td>65.56</td>
<td>1.74</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>NLP</td>
<td>26.25</td>
<td>40.19</td>
<td>1.53</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>EPP</td>
<td>35.25</td>
<td>67.17</td>
<td>1.91</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>33.06</td>
<td>57.64</td>
<td>1.74</td>
<td>1.74</td>
</tr>
<tr>
<td>18 June, 2002</td>
<td>MPP</td>
<td>8.64</td>
<td>14.31</td>
<td>1.66</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>NLP</td>
<td>15.73</td>
<td>22.98</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>EPP</td>
<td>14.72</td>
<td>21.83</td>
<td>1.48</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>13.03</td>
<td>19.71</td>
<td>1.51</td>
<td>1.51</td>
</tr>
<tr>
<td>25 July, 2002</td>
<td>MPP</td>
<td>19.31</td>
<td>26.40</td>
<td>1.37</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>NLP</td>
<td>13.81</td>
<td>17.83</td>
<td>1.29</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>EPP</td>
<td>28.89</td>
<td>46.51</td>
<td>1.61</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>20.67</td>
<td>30.25</td>
<td>1.46</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Note: MPP, Morning peak period; NLP, Noon lean period; EPP, Evening peak period

TABLE 3—Concentration of benzene and toluene with toluene to benzene ratio monitored at peak and lean periods of the day at East Arjun Nagar, Delhi

<table>
<thead>
<tr>
<th>Duration</th>
<th>(C_{\text{benzene}}) (\mu\text{g m}^{-3})</th>
<th>(C_{\text{toluene}}) (\mu\text{g m}^{-3})</th>
<th>(C_{\text{toluene}}/C_{\text{benzene}})</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPP</td>
<td>23.42</td>
<td>32.92</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>NLP</td>
<td>13.25</td>
<td>15.72</td>
<td>1.19</td>
<td>1.19</td>
</tr>
<tr>
<td>EPP</td>
<td>16.42</td>
<td>19.78</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Average</td>
<td>17.69</td>
<td>22.81</td>
<td>1.29</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Note: MPP, Morning peak period; NLP, Noon lean period; EPP, Evening peak period

The concentrations being in the order of \(< 10^{20}\) and \(10^{16}\) cm\(^3\) mole\(^{-1}\) s\(^{-1}\), respectively. Thus, their depletion in the atmosphere via these reactions is negligible. The only significant process for the atmospheric loss of these compounds is their photochemical reaction with OH radicals, having rate constants 1.23\(\times 10^{16}\) and 5.96\(\times 10^{12}\) cm\(^3\) mole\(^{-1}\) s\(^{-1}\) for benzene and toluene respectively. These reaction constants were shown to have negligibly small temperature dependence below 50°C\(^1\).

Average benzene and toluene concentrations (33.69-174.62 \(\mu\text{g m}^{-3}\)) were found in the vicinity of petrol pump at Preet Vihar location (Table 1). These compounds remain in higher concentration in the surrounding of petrol pump. Probably the major sources are emissions from motor vehicles and evaporation losses during the handling, distribution and storage of petrol, although benzene content in gasoline has been reduced (3% to 1%) since November 2000, in the national capital territory of Delhi\(^20\). Benzene\(^21\) is also found in gasoline in Europe and worldwide (up to 5%). The emission of benzene is dependent upon aromatic content of gasoline\(^21\).

Average benzene and toluene concentrations in ambient air at ITO (Table 2) ranged between 13.03 - 33.06 \(\mu\text{g m}^{-3}\) and 19.71 - 57.64 \(\mu\text{g m}^{-3}\), respectively, while benzene and toluene concentration at East Arjun Nagar (Table 3) were found to be 17.69 \(\mu\text{g m}^{-3}\) and 22.81 \(\mu\text{g m}^{-3}\), respectively. Gasoline consumption in Delhi has shown a growth (247%) during 1997-98 against 1980-81 as compared to diesel consumption growth (150% only) during the same period. In the petrol driven 2 wheelers, the emission of benzene is significant, because 20-30 percent of fuel comes out as unburnt hydrocarbons\(^19\). In view of this, the present study indicates that their levels in ambient air of Delhi are directly related to the intensity and magnitude of traffic character. Their concentrations are also indirectly related to dispersion, stability and wind speed\(^22\).

Maximum levels of benzene and toluene were found at Preet Vihar followed by ITO and East Arjun Nagar. Toluene had higher values in all the cases followed by benzene. Table 4 shows the benzene and toluene levels measured by thermal tube desorption method in various locations worldwide. A recent study in the urban air of Inzmir, Turkey also found toluene to be the most abundant VOC followed by benzene. Table 4 shows the benzene and toluene concentrations monitored in Delhi at residential area, traffic intersection and in vicinity of petrol pumps varied...
between 42 µg m$^{-3}$ to 195 µg m$^{-3}$, but the present levels (13.03-174.62 µg m$^{-3}$) have slightly decreased down perhaps due to betterment in fuel quality and other control measures being taken and implemented by the government$^{28}$. The average toluene to benzene ratio (Fig. 2) calculated for different sampling periods and sites indicate a good correlation between toluene and benzene at most of the sampling sites. In another study$^{29}$, toluene to benzene ratio in ambient air was about 2.0 near the roads with heavy traffic flow and 1.0-6.0 in a suburban area. The average ratio (1.29-1.74) in the present study is in good agreement with the previously reported values.

### Conclusions

Toluene to benzene ratio is more useful for the characterization of a given sampling site with respect to the proximity of vehicular emission sources than the absolute concentrations of related pollutants. Results indicate further detailed study in metropolitan city of Delhi and other metropolitan cities as well as the necessity of limit value to be laid down immediately for ambient air quality in India besides action plan to bring down the existing levels within target limit.

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### References


