



TECHNICAL NOTE

DETECTION OF AROMATIC HYDROCARBONS IN THE ATMOSPHERE
AT PPT LEVELS

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Abstract—A new method has been described and evaluated which will detect ppt levels of hydrocarbons in the atmosphere. An automatic GC was used with a concentrator and a photoionization detector to measure benzene, toluene and xylene. The values obtained in the Boston, MA area were in good agreement with the literature value. The BTX data were compared with simultaneous CO₂ data and some interesting features were observed. Good correlation was obtained with simultaneous CO₂ data during rush hour traffic and no correlation during the early morning hours when the BTX values would rise while the CO₂ values decreased to their ambient levels of 350 ppm.

Key word index: Benzene, toluene, xylene, traffic emissions.

1. INTRODUCTION

The recent Earth Summit in Rio underscores just how serious the environmental problems of the world really are (Driscoll, 1992). It is clear that we will need a better understanding of the extent of many of our present environmental problems if we are to make significant progress during this decade.

Hydrocarbons, along with oxides of nitrogen and ultraviolet light, combine in the atmosphere, in a complex manner, to form photochemical smog. To make matters worse, automotive sources emit several hundred different hydrocarbons (Manahan, 1991). Although the smog problems are well known in Los Angeles, CA; Denver, CO; and Mexico City, even Boston, MA can have a problem during the summer months (Anon., 1992).

The hydrocarbon situation in the U.S.A. has changed during the 1980s where aromatics have replaced tetraethyl lead in gasoline as octane enhancers. Transportation is a major source of emissions of benzene, toluene, ethyl benzene and xylenes (BTEX) (Warneck, 1988) and accounts for more than 70% of the total atmospheric emissions of hydrocarbons.

The most popular methods for continuous measurements of non-methane hydrocarbons have involved gas chromatographs which measure total hydrocarbons (direct injection) then methane (on a GC column) with a flame ionization detector (FID) (Villalobos, 1974). The non-methane hydrocarbons are obtained by difference between the two channels. Typical analysis times ranged from 5 to 10 min. Other variants involve the measurement of automotive related hydrocarbons such as ethylene and acetylene or conversion of the non-methane hydrocarbons to CO₂ then back to methane to remove adsorption problems due to heavier hydrocarbons. These analyses took 10–15 min. Another, simpler method described by Driscoll (1979) employed a photoionization detector (PID with a 10.2 eV lamp) with no column. Here methane and some light hydrocarbons are not detected since their ionization potentials are greater than 10.2 eV. The reading was continuous with a response time of 5 s.

Methods for collection of atmospheric hydrocarbons involve collection of a large volume (10³ l) of air over a period of time (8 h) on a solid sorbent to obtain average concentrations

of up to several hundred compounds for urban atmospheres (Stephens and Burleson, 1969). These samples are returned to the laboratory for analysis. A number of studies have shown that many of the volatiles can be lost during the process of sending samples to laboratories. The EPA reported in its Superfund program that > 50% of the samples returned to contract laboratories had no volatiles detected (Driscoll, 1993). In addition, some of the species may undergo additional chemical reactions during shipping and storage. Another method involves the collection of the air samples in canisters (6 l SUMMA passivated canister) and subsequent analysis on a laboratory GC equipped with several detectors: usually FID and ECD with the PID optional (EPA, 1989). This technique may be used to collect either grab samples (duration of 10–30 s) or time integrated samples (duration 12–24 h). A portion of the canister sample is passed through a cryogenic trap which is then heated to inject the compounds on the head of a capillary column. A temperature programmed analysis typically resolves over 40 compounds in about 30 min.

Although some of these methods can be quite sensitive, they are not easily automated to yield continuous results. Another technique developed at the University of Michigan (Mouradian *et al.*, 1991) with input from HNU Systems involves collecting an air sample at liquid nitrogen temperatures, then rapidly heating the collected sample and injecting this narrow band onto the head of a chromatographic column. The result is a rapid analysis (20 compounds in 20 s) with baseline separation. The collection and analysis is done on-site but the method is still manual. This technique is being evaluated by EPA for field (mobile lab) usage. Most of the chromatographic methods described in the literature for ambient hydrocarbons use a flame ionization detector (FID) but it would appear from the work of Hester and Meyer (1979) and others (Cox and Earp, 1982; Driscoll and Spaziani, 1976) that the photoionization detector (PID) has a number of advantages including sensitivity and selectivity.

Our approach has been to determine whether some simple modifications to an existing instrument (automatic GC) that employs a sensitive photoionization detector and a simple concentrator could be used to monitor selected hydrocarbons, in this case aromatics, in the atmosphere on a continuous and automatic basis. To achieve this, we had to develop a system which could handle samples and detect components in the parts per trillion (ppt) range. These results will be discussed in the following sections.

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2. EXPERIMENTAL

The instrument used for the hydrocarbon measurements was a modified Model 301-D gas chromatograph (HNU Systems, Inc., Newton, MA) which can be set up as an automatic analyser for sampling ambient or plant air (Driscoll *et al.*, 1988). The concentrator was installed in place of the sample loop in the standard 10 port fluidics configuration of the instrument. The concentrator consists of a silanized glass tube containing a solid sorbent (HNU SS # 300-VHC) wrapped in nichrome wire to provide heating. A Rate Transducing Diode (RTD) was inserted between the glass tube and the wire windings. The microprocessor in the GC was used to control the heating time for the desorber trap. The power was regulated to provide a rapid and reproducible temperature ramp for the desorption process. This setup produces sharp chromatographic peaks due to rapid and uniform desorption and therefore a narrow injection band width. To control the quantity of sample introduced into the trap, a sample pump was started for a fixed amount of time at a flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$. A needle valve was used to ensure that the sample flow rate could be controlled. After the desired sample time, a solenoid valve was opened and the trap was flushed with nitrogen to purge air and water.

GC analyses were carried out on a 0.53 mm, 15 m, $5 \mu\text{m}$, NB-30 capillary column (HNU Systems, Inc., Newton, MA). The column flow rate was $15 \text{ cm}^3 \text{ min}^{-1}$. The initial column temperature was 60°C for 1 min and ramped to 110°C at $15^\circ\text{C min}^{-1}$ and held at 110°C until the end of the analysis. The detector was a PID with a 10.2 eV lamp (HNU Systems, Inc., Newton, MA). The carrier gas was Ultra High Purity Nitrogen (Liquid Carbonic, Medford, MA).

The ppb level certified standard calibration gas was obtained from Scott Specialty Gases (Plumbsteadville, PA) and contained hydrocarbon levels of benzene 12.4 ppb, toluene 12.0 ppb, chlorobenzene 12.0 ppb, *o*-xylene 12.7 ppb, and *m*-dichlorobenzene 12.0 ppb. The 1 ppm level of standard gas containing benzene, toluene and xylene was also obtained from Scott Specialty Gases. All data collection was done on a Spectra-Physics 4270 Integrator (Spectra Physics, Santa Clara, CA). The start of the integrator was controlled by the GC microprocessor and was linked to the inject cycle. Data was then manually entered into a Lotus 123 (Cambridge, MA) spreadsheet in order to observe trending information. Although this method of data collection was sufficient for short-term studies, it is difficult to routinely do this for a continuous monitor because of the large quantity of data. In future work, an RS232 port will be used to transfer the data to the computer automatically.

The CO_2 measurements were made with an HNU Systems model 61 electrochemical monitor. The output from the CO_2 monitor was fed into a PSION (Boston, MA) datalogger and transferred into a computer on a weekly basis. Display of the data was accomplished through Lotus 123. The measurements were taken every 5 min on a continuous basis.

3. RESULTS AND DISCUSSION

To ensure the accuracy of the concentrator at ppb levels, a standard tank of benzene 12.4 ppb, toluene 12.0 ppb, chlorobenzene 12.0 ppb, *o*-xylene 12.7 ppb, and *m*-dichlorobenzene 12.0 ppb was used during the initial tests. This proved invaluable for the evaluation of the concentrator/GC as a monitor for sub-ppb levels of the above mentioned compounds. The sample was drawn off a split sample line (with one side vented to the atmosphere) from the standard calibration cylinder. This avoided the problem of trying to get the standard to the analyser without contamination from a sample bag, a difficult feat at the part per trillion level. This also prevented excess flow of the calibration standard into the trap.

The instrument was calibrated and allowed to run for 4 d on ambient air. The same standard was then analysed under the identical conditions. The results of this analysis showed that the stability of the device was good. Compounds such as benzene, toluene and *m*-dichlorobenzene showed a small change after 4 d, about 15% or less, while the results for the *o*-xylene were somewhat higher: ca. 24%. The stability of the retention time during this time period was excellent since all retention times were within 1% or less.

The reproducibility [coefficient of variation (CV)] of the standard ppb gas for five sequential analyses varied from 4 to 7.7% as shown in Table 1 below.

Dilutions of the low ppb standards demonstrated that levels in the low parts per trillion could be analysed with this instrument with some modification. To perform this analysis, it was necessary to subtract the baseline of a blank run. The results are shown in Fig. 1. The reason for the blank was that low part per trillion levels of BTX (perh. ps in the UHP nitrogen gas cylinder used for dilution), as well as several unidentified compounds, were interfering with the analysis. When we ran tests on the UHP nitrogen gas cylinders, we found significant (ppt) levels of these aromatic compounds in

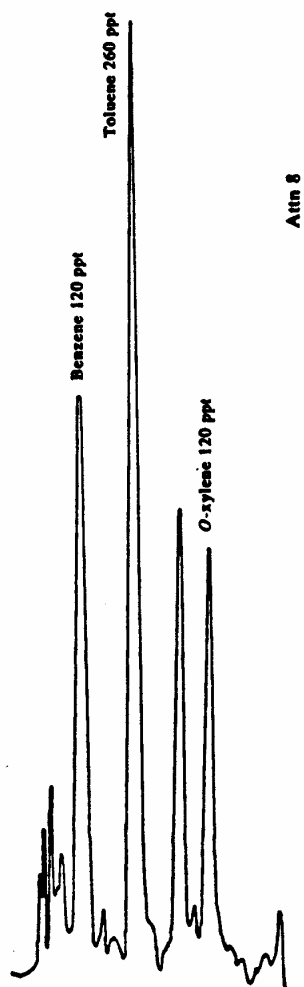


Fig. 1. PPT standard with concentrator/desorber.

the gas (toluene, 50 ppt; xylene, 200 ppt; benzene unknown). Typical zero gas has a specification of <0.1 ppm of hydrocarbons. While this is adequate for most studies, it is a serious problem when one is analysing low ppb or ppt levels of gases.

To determine the range and efficiency of the concentrator, a certified gas standard of 1 ppm benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene was used. This 1 ppm level was selected as a result of the capability of the GC to quantify the unconcentrated sample on direct injections as well as the concentrated analysis. Since there was a shift in retention time between direct injection and the concentrator run, the peak area data from the Spectra-Physics was used for comparison. One milliliter of a 1 ppm standard was injected by syringe and analysed. The 1 ppm standard was then sampled at a rate of 100 ml min⁻¹ for 2 min, an equivalent of a 200 ml injection volume. The results in Table 2 below indicate that the concentrator is quantitatively concentrating the sample since the peak areas for the concentrated sample were approximately 200-times greater than the directly injected sample of 1 ml. It also demonstrates the excellent range of the concentrator.

Extrapolation of the peak areas for each analysis provided results within 20% of the correct value for each tank. The 20% discrepancy could be explained by an inaccuracy in metering the gas standard.

Now that the stability and other parameters of the system were satisfactory, we started an evaluation to determine the aromatic hydrocarbon content of ambient air. A typical chromatogram for ambient air is shown in Fig. 2. More than two dozen compounds were detected in this chromatogram. In order to simplify the analysis, the trap material was selected so that many of the light hydrocarbons would pass through the concentrator. The number of light hydrocarbons in the air is significant. The PID with the 10.2 eV lamp also helped since it does not respond to many of the light hydrocarbons (Driscoll and Duffy, 1987).

The system was run in the continuous mode over a period of one month. The data for a typical day period is plotted in Fig. 3 and the observed trends are interesting. At times, all levels for BTX correlated and at other times, the toluene and xylene increased but the benzene peak remained constant. This may indicate levels of solvent use in our area since it is

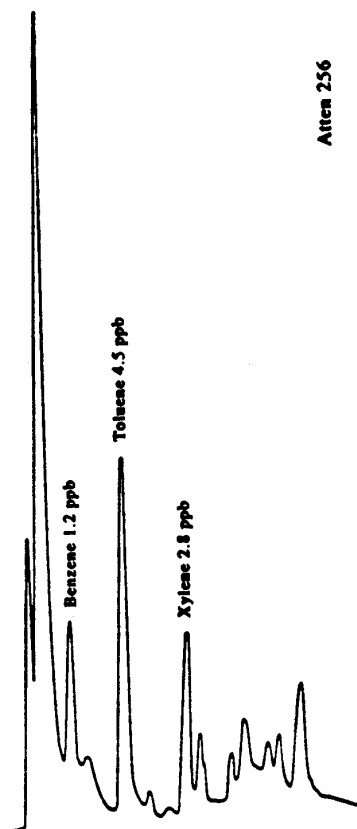


Fig. 2. Typical ambient air trace with concentrator/desorber.

Table 1. Reproducibility for BTX at ppb levels

Run	Benzene	Toluene	Xylene
1	12.40	12.00	12.70
2	11.80	11.35	11.92
3	11.59	10.87	11.34
4	11.41	10.42	10.78
5	11.00	9.90	10.18
Average	11.64	10.91	11.38
Std dev.	0.46	0.73	0.88
CV (%)	4.0	6.6	7.7

Table 2. Comparison of the peak areas for a 1 ppm sample before and after concentration

Component	Direct injection (1 ml)	Concentrated sample (200 ml)
Benzene	2.2 × 10 ⁴	4.9 × 10 ⁶
Toluene	2.0 × 10 ⁴	5.2 × 10 ⁶
<i>m/p</i> -xylene	5.2 × 10 ⁴	12.9 × 10 ⁶
<i>o</i> -xylene	2.1 × 10 ⁴	4.9 × 10 ⁶

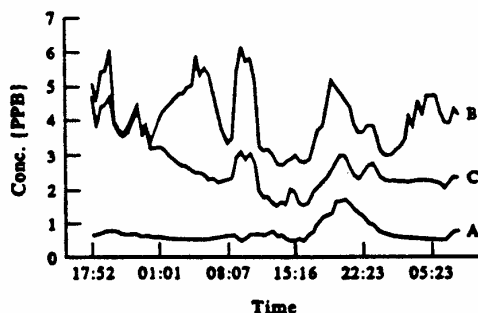


Fig. 3. Continuous air analysis (A = benzene; B = toluene; C = xylenes).

industrialized. Benzene is not used as a solvent and the source is only from automotive emissions. The levels found for benzene were approximately 950 ppt, for toluene 5 ppb, and total xylenes 4 ppb. These levels agreed with earlier data reported for the Boston area (Warneck, 1988). The ranges for these compounds for the one-month period are shown in Table 3.

The data shown in Fig. 3 is typical of many runs where increases in BTX during the morning and evening rush hour

Table 3. Concentration ranges for Newton, MA over a one-month period

Component	Range (ppb)
Benzene	0.5-1.6
Toluene	2.8-6.1
Xylene	1.6-4.8

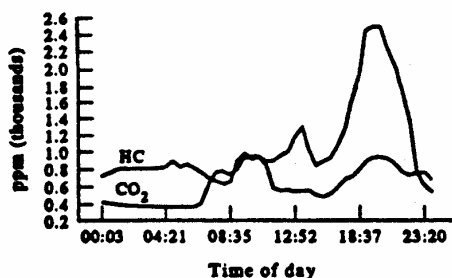


Fig. 4. Comparison of CO₂ and BTX vs time of day.

were observed. The presence of a nearby shopping area (approximately 1/4 mile) extended the length of the morning rush hour and the late afternoon rush hour peaked at 8 p.m. instead of an earlier time which would have been typical. One unusual aspect of the data was the increase in BTX during the early morning (1-5 a.m.) when there was no automotive traffic.

After the trap had run for the one-month period, concentration of the low ppb standard was performed. The results showed that the trap still concentrated the sample with the same efficiency that it had one month earlier. The results from the continuous run were very encouraging because they showed that the trapping material did not degrade despite the extended use. This was especially important for continuous operation without requiring frequent changing of the trap material. The trap material appeared to improve with continuous usage and showed fewer spurious peaks during calibration runs. Also, no decrease in the efficiency of the trap was observed over the test period.

In Fig. 4, we compare the results for CO₂ (ppm) with the total BTX (ppb) values which were obtained by summing the individual chromatographic values for each point. The BTX results were described earlier and during the long "rush hour" traffic (8:30 a.m.-10:30 p.m.) which included some aberration from the nearby mall, the CO₂ data shows a high correlation ($r^2 = 0.75$) with total BTX indicating that the data is from the same source. If the entire 24-h BTX data is compared with CO₂, the correlation coefficient ($r^2 = 0.03$) is quite poor. During the late evening, the CO₂ drops to the ambient level of 350 ppm while the BTX values mysteriously rise.

4. CONCLUSIONS

This work demonstrated that a continuous monitor could be developed based on a GC and concentrator system to measure down to ppt levels of aromatics in the atmosphere.

The trap material and PID detector were selected in order to optimize the analysis for components such as benzene (C₆), toluene (C₇) and the xylenes (C₈), (BTX). These compounds are by-products of gasoline combustion and are good markers of automobile pollution. The ambient levels for the Boston area were reported at approximately 3 ppb in the literature. Detection levels greater than ten times lower than these were easily achieved with the current experimental configuration.

Data from Warneck (1988) indicate that if we examine sources for BTX, we find that essentially all of the benzene emissions come from transportation, while approximately 40% of the toluene and ethyl benzene emissions are from solvent usage. By taking the benzene to toluene ratios for industrial areas, one would be able to estimate contribution of both transportation and solvent usage to the pollution of the atmosphere. The ability to monitor these trends would be a useful tool for both regulators and industry alike. If a wider number of species are monitored on a continuous or semicontinuous basis, each measurement can provide atmospheric scientists with some information which may help solve environmental problems.

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