

Accuracy of photo-ionisation detectors at high concentrations of volatile organic compounds

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Accuracy of photo-ionisation detectors at high concentrations of volatile organic compounds

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This project was designed to develop a system which will allow the generation of vapour from selected VOC liquids at higher concentrations than can be supplied commercially in gas cylinders or from existing HSL systems, and to use this to investigate the accuracy of PIDs at these high concentrations.

Attempts to create a static system of vapour production were unsuccessful.

Attempts to create a dynamic system of vapour production were moderately successful, the maximum concentration of xylene vapour generated being 1720 ppm and the maximum concentration of toluene vapour generated being 3220 ppm. This method increased the range of xylene vapour concentrations available by more than 100%. It did not, however, significantly increase the range of toluene vapour concentrations. The output of the dynamic vapour generation system is linear and repeatable.

The accuracy of the PID at higher xylene concentrations was within 1% of the generated concentration and well within the documented instrumental tolerances of $\pm 10\%$ of the reading. The worst case relative deviation in the results of 1.4% suggests that this method of vapour generation will be of a satisfactory level of consistency to allow the investigation of the operational characteristics of a PID monitor at concentrations up to the limit of the generation system.

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EXECUTIVE SUMMARY

Photo-ionisation detectors (PIDs) are commonly used to monitor low concentrations of volatile organic compounds (VOCs) (up to 10% of range) with acceptable accuracy (eg in the petrochemical industry or industrial paint stripping facilities etc). However, previous investigations into concentrations of some VOCs using PID technology showed that, at high concentrations, yet below 50% of the operating range of the detectors, calibration factors could be significantly different from documented values.

The aims of this project were to extend the investigation into the accuracy of PIDs at high concentrations of VOCs, including concentrations approaching the Lower Flammability Limit (LFL); and to develop a facility which would allow the controllable, accurate, repeatable generation of vapour from selected liquids at higher concentrations than can be supplied commercially in gas cylinders.

A static system of VOC vapour production for generating concentrations of VOCs higher than those available commercially in cylinders was unsuccessful. This is due to the fact that the concentration of the VOC vapour cannot be easily controlled, and the effect of the concentration produced on the operation of the monitors is uncertain.

A dynamic system of VOC vapour production for generating concentrations of VOCs higher than those available commercially in cylinders was moderately successful, producing linear calibrated, repeatable, higher vapour concentrations of toluene and xylene than those available commercially in cylinders. This will allow the investigation of the operational characteristics of a PID monitor to concentrations up to the saturation limit of the generation system.

The maximum concentration of xylene vapour generated by the dynamic system was 1720 ppm which is 115% greater than the maximum concentration of 800 ppm available commercially in cylinders, but still only 20% of the maximum predicted concentration of 8,700 ppm at an ambient temperature of 20 °C and pressure of 1 bar. The maximum concentration of toluene vapour generated by the dynamic system was 3220 ppm, which is 7% greater than the maximum concentration of 3,000 ppm available commercially in cylinders, but still only 11% of the maximum predicted concentration of 29,000 ppm at an ambient temperature of 20 °C and pressure of 1 bar. Therefore the dynamic method of vapour generation has increased the range of xylene vapour concentrations available by more than 100%. It did not, however, significantly increase the range of toluene vapour concentrations.

The worst case relative variability in any given detected concentration of 1.4% of the average concentration suggests that this method of vapour generation will be of a satisfactory level of consistency.

The concentrations of the vapours at which the operational characteristics of the monitors could be affected could not be determined as the maximum possible generated concentration (saturation) was reached before any such effect was evident.

VOC concentrations approaching the lower flammability limit could not be achieved because liquid droplets formed on the inside of the evaporation chamber, resulting in inconsistent concentration readings.

The system produced in this investigation has the following advantages and disadvantages when compared to existing methods of vapour supply:

- Gas bottles: Concentration certified, more accurate and more consistent, but not as cost effective or flexible as the new system
- Existing HSL syringe pump system: Concentration does not have range or consistency of the new system
- Bubbler systems: Safety concerns due to lack of control and high probability of concentrations around LEL being produced

None of the above existing systems can provide such a wide range of accurate and cost effective VOC concentrations as the new system.

The dynamic vapour generation system was used to investigate the operational characteristics of a PID monitor at the higher concentrations of xylene achievable. The concentrations detected by the PID were found to be within 1 % of the actual generated concentration monitored using the more accurate FID. The variability of each of the concentrations of both toluene and xylene detected by the PID was comparable to that of the FID at those concentrations. The dynamic vapour generation system should therefore allow the investigation of the operational characteristics of a PID monitor at concentrations up to the limit of the generation system.

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1. INTRODUCTION

Volatile organic compounds (VOCs) are commonly encountered in industry as they widely occur in the petrochemical industries and are used as industrial solvents and cleaners. As well as being flammable, many VOCs exert a narcotic effect and they can be toxic at lower concentration levels. It is therefore important to monitor VOCs over a wide concentration range to mitigate both safety and health risks.

Photo-ionisation detectors (PIDs) are commonly used to monitor low concentrations of volatile organic compounds (VOCs) (up to 10% of range) with acceptable accuracy (eg in the petrochemical industry or industrial paint stripping facilities etc). They have a wider concentration range than both catalytic and infrared explosimeters used to monitor for flammable risk. However, previous investigations undertaken at HSL into concentrations of some VOCs using PID technology showed that, at high concentrations, yet below 50% of the operating range of the detectors, PID calibration factors could be significantly different from documented values. Measurement of higher VOC concentrations is required in certain situations, eg liquid/aerosol releases, and calibration of the PIDs around these levels is limited to less than 50% of the ranges of the PIDs by the saturation vapour pressure of the vapour. It is therefore necessary to calibrate the monitors accurately over this extended range, particularly when concentration levels approach potentially flammable/explosive levels ie around the lower explosive level (LEL).

The aims of this project were to extend the investigation into the accuracy of PIDs at high concentrations of VOCs, including concentrations approaching the Lower Flammability Limit (LFL); and to develop a facility which would allow the controllable, accurate, repeatable generation of vapour from selected liquids at higher concentrations than can be supplied commercially in gas cylinders.

These were to be achieved by

1. building a permanent dedicated vapour generation system;
2. testing the accuracy of the vapour generation system at lower concentrations;
3. determining the maximum vapour concentration which can be generated at a given ambient temperature and pressure;
4. testing the accuracy of PIDs to selected VOCs using the vapour generation system;
5. utilising the vapour generator to calibrate VOC monitors at higher concentrations of VOCs than currently possible.

Two vapour generation systems were investigated:

1. A static vapour production system; ie no air flow ^[1] in which a controlled volume of liquid VOC was pooled into an airtight chamber and allowed to vaporize until all of the liquid had evaporated or the atmosphere in the chamber was saturated
2. A dynamic vapour production system ie involving air flow ^[2] in which the syringe pump-based system already used in HSL to produce lower concentrations of vapours was modified to investigate the cut off level at which the liquid no longer vaporizes (saturated vapour concentration), and the accuracy and repeatability of this new system.

The accuracy of a PID-based monitor at vapour concentrations higher than those available commercially in gas cylinders was then investigated using the most suitable vapour generation system of the two described above.

2. STATIC VAPOUR PRODUCTION SYSTEM

2.1 GENERAL

The static system of vapour production included the following:

- Vaporization effected by pooling a controlled volume of liquid into a static controlled volume of air in an airtight chamber and allowing vaporization to occur until either all of the liquid has evaporated or the atmosphere in the chamber has reached its saturated vapour concentration;
- A calibrated sensor positioned in the system to monitor the vapour concentration as vaporization occurs;
- When the required vapour concentration has been attained, the instrument to be calibrated connected to the outlet of the chamber;
- A collapsible bag included in the chamber in such a way that it can be inflated from outside the chamber, the effect of which is twofold:
 - to allow the vapour extracted by pumped monitors to be replaced by inflating the bag at the same flow rate and preventing a negative pressure build up which will cause the instrument pump to stall;
 - inflating the bag at a controlled flow rate to expel the vapour from the chamber for use with monitors without pumps;
- Concentrations produced initially at levels comparable to those which are commercially available. This will allow the real time monitors to be calibrated and checked at these concentrations;
- Concentrations then produced at levels higher than those which are commercially available and the real time monitors and concentrations to be calibrated and checked using a calibrated flame ionization detector (FID);
- The effect of temperature on the system to be investigated.

Two common VOC liquids, xylene and toluene were investigated. The relevant exposure^[3] and explosive^[4] limits, and vapour pressures of each at an ambient temperature of 20 °C and pressure of 1 bar (calculated using the Antoine equation, see Appendix 1, Section 8.1 for calculations) are shown in Table 2.1.

Table 2.1: Properties of xylene and toluene

| VOC | WEL (ppm) | STEL (ppm) | LEL (ppm) | Saturated vapour pressure (bar) | Max vapour concentration (%) |
|---------|-----------|------------|-----------|---------------------------------|------------------------------|
| Toluene | 50 | 100 | 10,000 | 0.029 | 2.90 |
| Xylene | 50 | 100 | 10,000 | 0.0087 | 0.87 |

Two VOC monitors based on photo-ionisation detection (PID) technology were used to monitor the concentration of vapour in the static system tests.

2.2 METHODOLOGY

The monitors were calibrated to the relevant certified values of the highest commercially available nominal concentrations of 800 ppm of xylene (certified concentration of 799 ppm) or 3,000 ppm toluene (certified concentration of 2975 ppm) vapour before each test. The calibration was checked before and immediately after the tests, and after cleaning the PID lamps at the end of the tests, to investigate any contamination effects from the vapour.

For the tests the monitors were positioned side by side in the centre of the 12 litre air tight vessel as shown in Figure 2.1, which was located in a fume cupboard. The probes from the monitors were directed towards the centre of the vessel below the monitors, where a 10 mm diameter dish containing the liquid VOC approximately 5 mm in depth was placed in the bottom of the vessel as shown in the diagram in Figure 2.2.

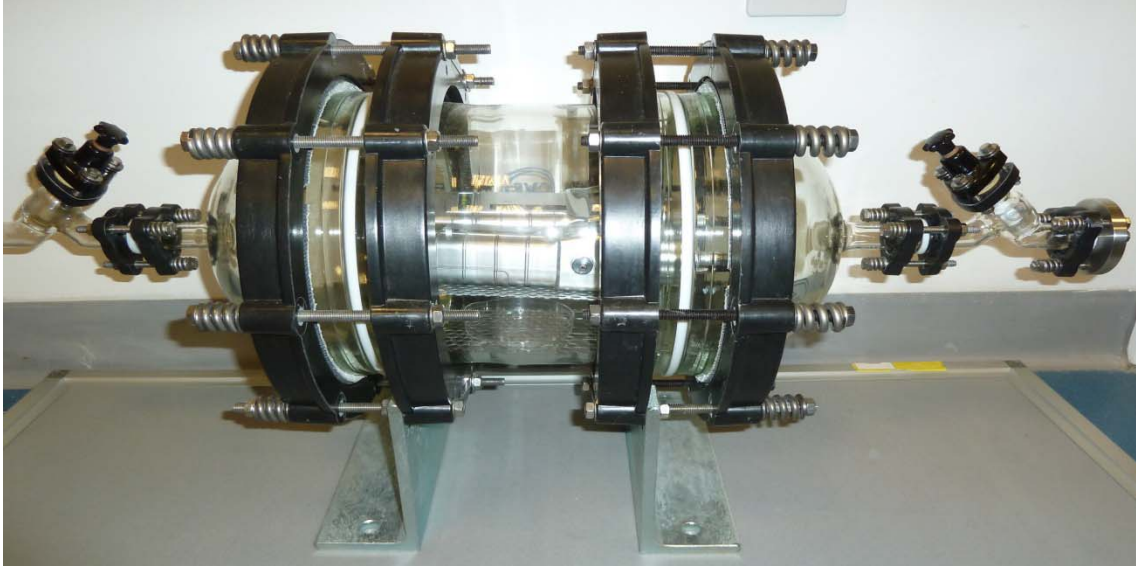


Figure 2.1: Monitors positioned in the air tight vessel

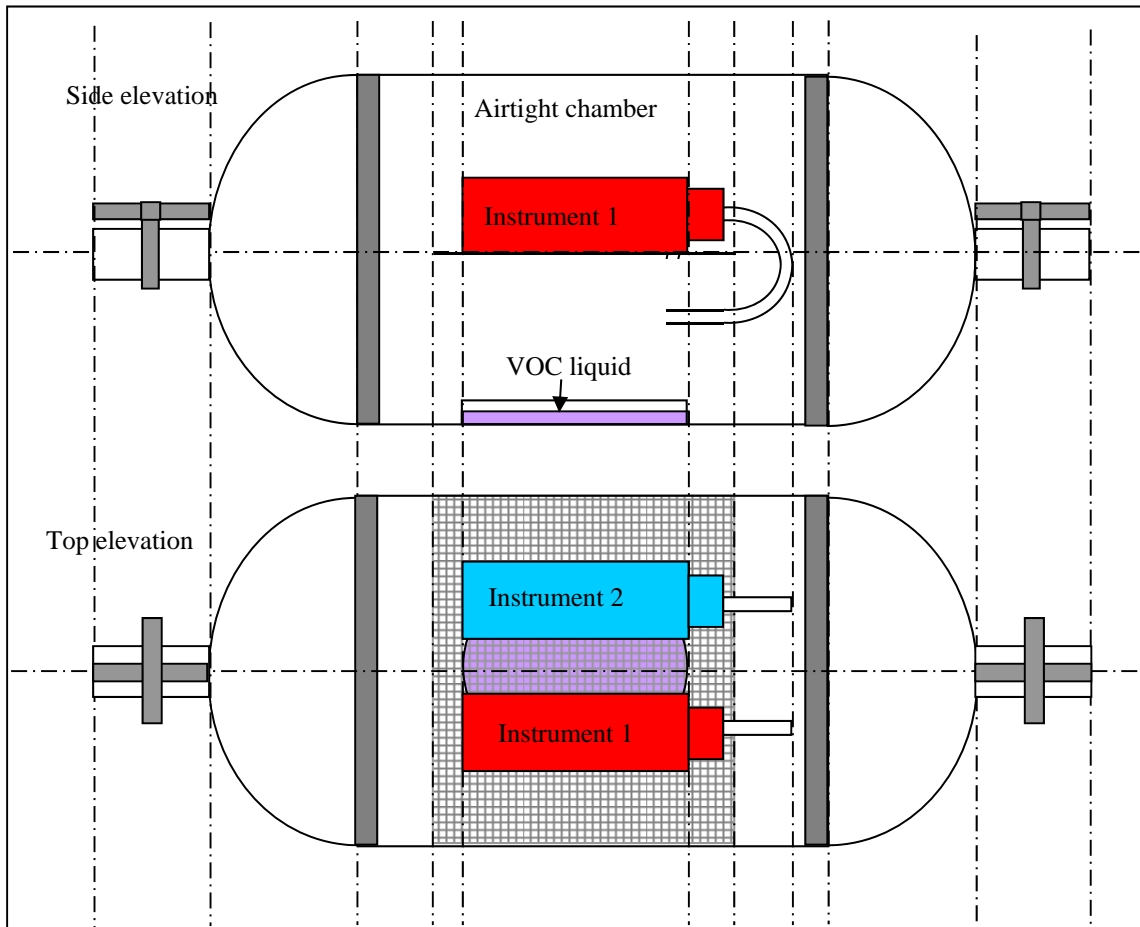


Figure 2.2: Diagram of monitors and VOC liquid positioned in the air tight vessel

The vessel was immediately sealed and the concentration of the vapour left to equilibrate.

Each set of tests was performed three times for each type of vapour to determine the repeatability of the set up.

Tests were also carried out with the probes positioned to sample the concentration of vapour in various locations in the vessel.

2.3 RESULTS

2.3.1 General

The start of the exposure times in Figures 2.3 and 2.4 include the times taken to close and seal the air tight vessel, during which the monitors were exposed to the vapour emanating from the liquid, ie the vessel may not have been fully air tight during the first five minutes of exposure. To allow the results using each of the vapours to be compared, analysis was performed on data observed over the first four hours of exposure in each case.

Vapour concentration was reasonably consistent in all locations inside the vessel in both the toluene and xylene tests. When the vessel was opened at the end of the tests very little of the VOC had evaporated, but when removed from the vessel and placed in the fume cupboard it evaporated fully within approximately two hours.

2.3.2 Toluene evaporation

The profiles of the concentrations of toluene vapour detected by the monitors in the airtight chamber during evaporation of the liquid toluene are shown in Figure 2.3.

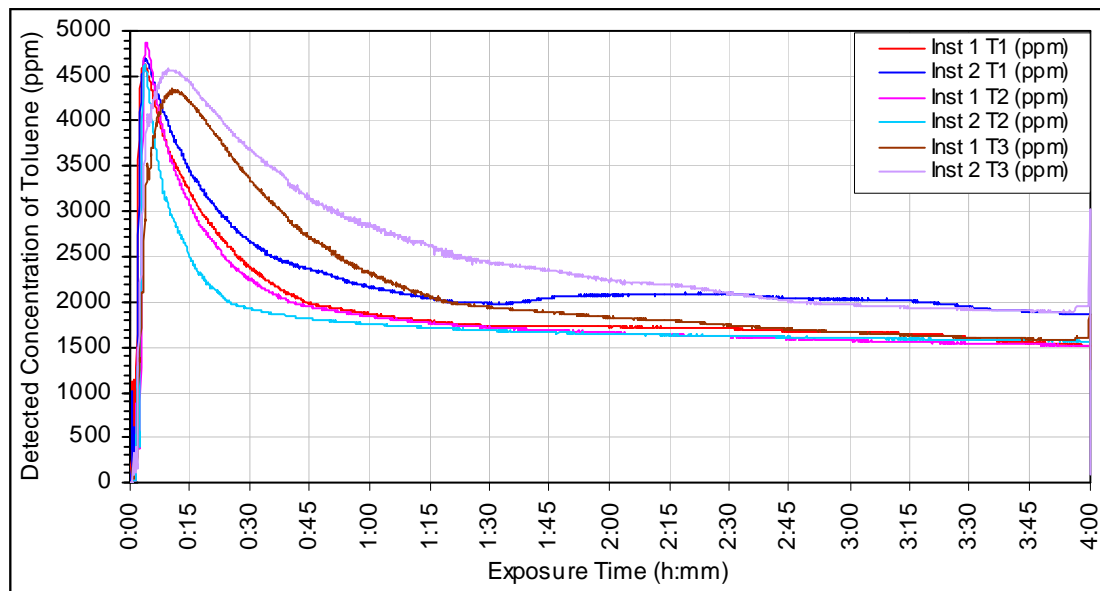


Figure 2.3: Profile of toluene concentration detected during vaporization

In all of the tests the concentrations detected by each of the monitors peaked within ten minutes of the monitors and the toluene liquid being placed in the vessel. In the first two tests the concentration of toluene vapour detected by each of the monitors peaks within the first four minutes. The time of around nine minutes taken for the monitors to reach a maximum in the third test may be due to extra time being taken when sealing the vessel due to difficulties in fitting the air tight cover.

The concentrations detected by each of the monitors then reduce at a rate of between 35 ppm per minute (instrument 2, test 3) and 90 ppm per minute (instrument 2, test 2) for approximately one hour, and then tend towards a consistent value over remaining three hours of the test.

The maximum, minimum, and reduction in concentrations detected by each instrument in each test over the four hour period analysed are shown in Table 2.2.

Table 2.2: Maximum, minimum, and reduction in concentrations detected by each instrument

| Instrument & Test No | Maximum detected concentration (ppm) | Detected concentration after 4 hrs (ppm) | Reduction in detected concentration (ppm) |
|----------------------|--------------------------------------|--|---|
| Inst 1 Test 1 | 4634 | 1524 | 3110 (67%) |
| Inst 2 Test 1 | 4689 | 1873 | 2816 (60%) |
| Inst 1 Test 2 | 4869 | 1518 | 3351 (69%) |
| Inst 2 Test 2 | 4623 | 1569 | 3054 (66%) |
| Inst 1 Test 3 | 4362 | 1583 | 2778 (64%) |
| Inst 2 Test 3 | 4571 | 1898 | 2672 (58%) |

The pre-exposure, post exposure, and post lamp cleaning calibration checks and reduction in signal are shown in Table 2.3.

Table 2.3: Pre-exposure, post exposure, and post lamp cleaning calibration checks and reduction in signal for each instrument

| Instrument & Test No | Calibration check pre-exposure (ppm) | Calibration check post exposure (ppm) | Reduction in signal (ppm) | Calibration check post lamp clean (ppm) |
|----------------------|--------------------------------------|---------------------------------------|---------------------------|---|
| Inst 1 Test 1 | 2960 | 1350 | 1610 (54%) | 2780 |
| Inst 2 Test 1 | 2940 | 2070 | 870 (30%) | 3000 |
| Inst 1 Test 2 | 2930 | 1450 | 148 (51%) | 3100 |
| Inst 2 Test 2 | 3000 | 1930 | 1070 (36%) | 3000 |
| Inst 1 Test 3 | 2930 | 1600 | 1330 (45%) | 3060 |
| Inst 2 Test 3 | 2930 | 2410 | 520 (18%) | 2760 |

The results suggest that the toluene begins to vaporize very quickly. As the vessel had been proved air tight prior to the start of the tests, the reduction in detected concentrations after the maxima are reached are most likely to be due to contamination of the optics in the instrument by the high concentration of toluene in the vapour, causing them to be less sensitive. The fact that the concentrations detected in the post-exposure calibration checks had also reduced, and that the cleaning of the optics returned the detected concentrations to levels comparable to the pre-exposure calibration checks seems to confirm this.

2.3.3 Xylene evaporation

The profiles of the concentration of xylene vapour detected by the monitors in the airtight chamber during evaporation of the liquid xylene are shown in Figure 2.4.

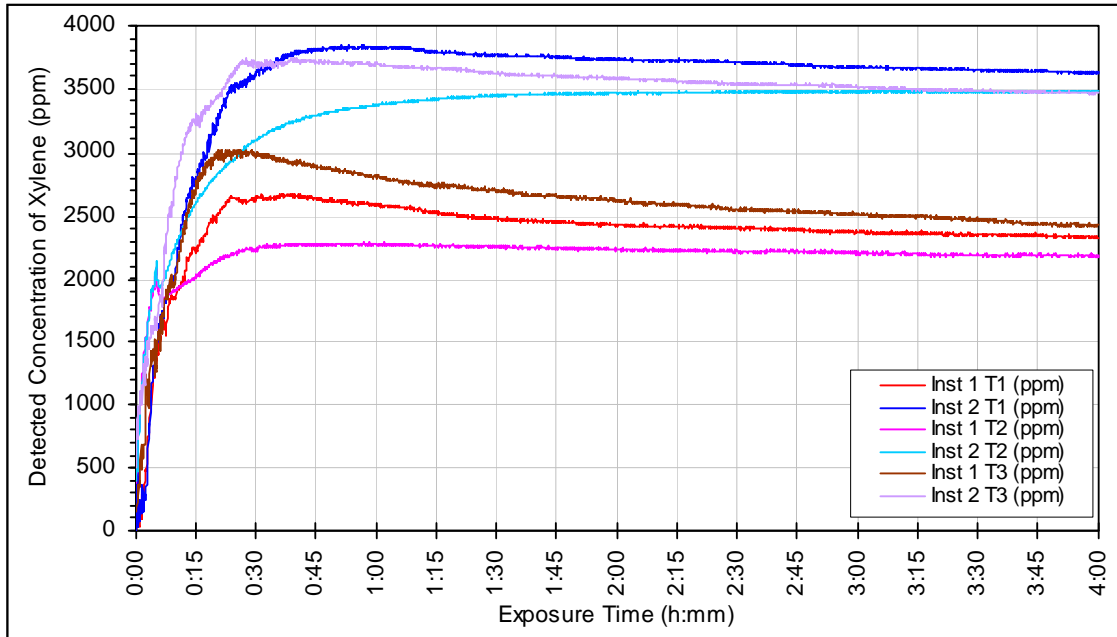


Figure 2.4: Profile of xylene concentration detected during vaporization

In all of the tests the concentrations detected by each of the monitors reach maxima within approximately 45 minutes, and then tend to remain close to that value reducing by between 1% (instrument 2, test 2) and 20% (instrument 1, test 3) over the remaining duration of the tests. The difference in concentrations detected by the two monitors is consistent, which suggests that this difference is due to a mis-match between the output of the PID lamp and the signal processing aspect of the monitors, at concentrations much higher than the calibration concentration.

The maximum, minimum, and reduction in concentrations detected by each instrument in each test over the four hour period analysed are shown in Table 2.4.

Table 2.4: Maximum, minimum, and reduction in concentrations detected

| Instrument & Test No | Maximum detected concentration (ppm) | Detected concentration after 4 hrs (ppm) | Reduction in detected concentration (ppm) |
|----------------------|--------------------------------------|--|---|
| Inst 1 Test 1 | 2681 | 2391 | 362 (14%) |
| Inst 2 Test 1 | 3847 | 3615 | 232 (6%) |
| Inst 1 Test 2 | 2290 | 2170 | 120 (5%) |
| Inst 2 Test 2 | 3490 | 3466 | 24 (1%) |
| Inst 1 Test 3 | 3034 | 2416 | 618 (20%) |
| Inst 2 Test 3 | 3743 | 3457 | 286 (8%) |

The pre-exposure, post-exposure, reduction in, and post-lamp cleaning calibration checks are shown in Table 2.5.

Table 2.5: Pre-exposure, post exposure, reduction in, and post lamp cleaning calibration checks

| Instrument & Test No | Calibration check pre-exposure (ppm) | Calibration check post exposure (ppm) | Reduction in calibration check (ppm) | Calibration check post lamp clean (ppm) |
|----------------------|--------------------------------------|---------------------------------------|--------------------------------------|---|
| Inst 1 Test 1 | 805 | 612 | 193 (23%) | 840 |
| Inst 2 Test 1 | 811 | 751 | 60 (7%) | 805 |
| Inst 1 Test 2 | 790 | 658 | 132 (17%) | 688 |
| Inst 2 Test 2 | 795 | 755 | 40 (5%) | 755 |
| Inst 1 Test 3 | 800 | Not performed | NA | Not performed |
| Inst 2 Test 3 | 800 | Not performed | NA | Not performed |

As with the toluene tests the results suggest that the xylene begins to vaporize very quickly, but as it is not as volatile as toluene and has a lower vapour pressure, it does not vaporize as readily or to the same saturation level, resulting in lower maxima and longer exposure times to reach those maxima. The reduction in detected concentrations after the maxima are reached may be due to contamination of the optics in the instrument. Alternatively, it may be that (as the reduction in detected concentration in most cases is so small) the actual saturation concentration for the conditions inside the vessel had been reached and is below the level at which the optics are affected, and the readings from the monitor were accurate. However, the fact that the concentrations detected in the post-exposure calibration checks had also reduced, and that the cleaning of the optics returned the detected concentrations to levels comparable to the pre-exposure calibration checks seems to agree with the initial assumption. The smaller fractional decrease in detected concentration when compared to the toluene tests may be due to the lower vapour pressure leading to a lower saturation level of xylene, and therefore less xylene vapour in the atmosphere to affect the optics.

The attainment of the predicted saturation concentration for the vapours at an ambient temperature of 20 °C and pressure of 1 bar (toluene: 29,000 ppm, xylene 8,700 ppm) could not be confirmed by the results in either set of tests due to the possible contamination of the optics in both cases, but the fact that most of the VOC liquid was still in the dish after 4 hrs, and that it later totally evaporated within 2 hrs of being placed in the air stream in the fume cupboard, suggests that a saturation level for the system had been reached in both cases. However, due to the restrictions resulting from a small enclosed volume these saturation levels may not have been the same as the predicted values.

As the concentration of the VOC vapour cannot be easily controlled in this method of production, and as the effect of the concentration produced on the operation of the monitors is uncertain, this method was deemed unsuitable to be utilized as a generic vapour production system.

3. DYNAMIC VAPOUR PRODUCTION SYSTEM

3.1 GENERAL

The dynamic vapour production system included the following:

- A FID, which detects concentrations of VOCs in real time used as an integral part of the system to monitor and display the concentration of vapour produced.
- Vaporization effected by introduction of a liquid over a range of flow rates controlled via a syringe pump, and air over a range of flow rates controlled via a mass flow controller (MFC) into a mixing chamber over a range of temperatures.
- Experience using a similar set up at HSL suggested the range of settings over which the tests should be undertaken to achieve the optimum vaporization rate
- Concentrations to be produced initially at levels comparable to those which are commercially available in order to allow the FID to be calibrated and checked at these concentrations
- If the relationship between the mixture settings and the detected concentration is found to be linear at these commercially available concentrations, while the relationship remains linear as the mixture setting is increased, the concentration detected by the FID will be deemed acceptable.

VOC liquids, xylene and toluene were again investigated. The relevant properties of each are shown in Table 3.1 ^[5].

Table 3.1: Properties of xylene and toluene

| VOC | Boiling Pt (°C) | Molecular Wt |
|---------|-----------------|--------------|
| Toluene | 110.6 | 92.14 |
| Xylene | 144.4 | 106.17 |

Two VOC monitors, one based on FID and one based on PID technology were used to monitor the concentration of vapour in the dynamic system tests.

3.2 METHODOLOGY

The dynamic vapour production system was designed in house, a plan and a photograph of which are shown in Figure 3.1 and 3.2 respectively. See Appendix 2 (Section 8.2) for complete list of equipment and purchase details.

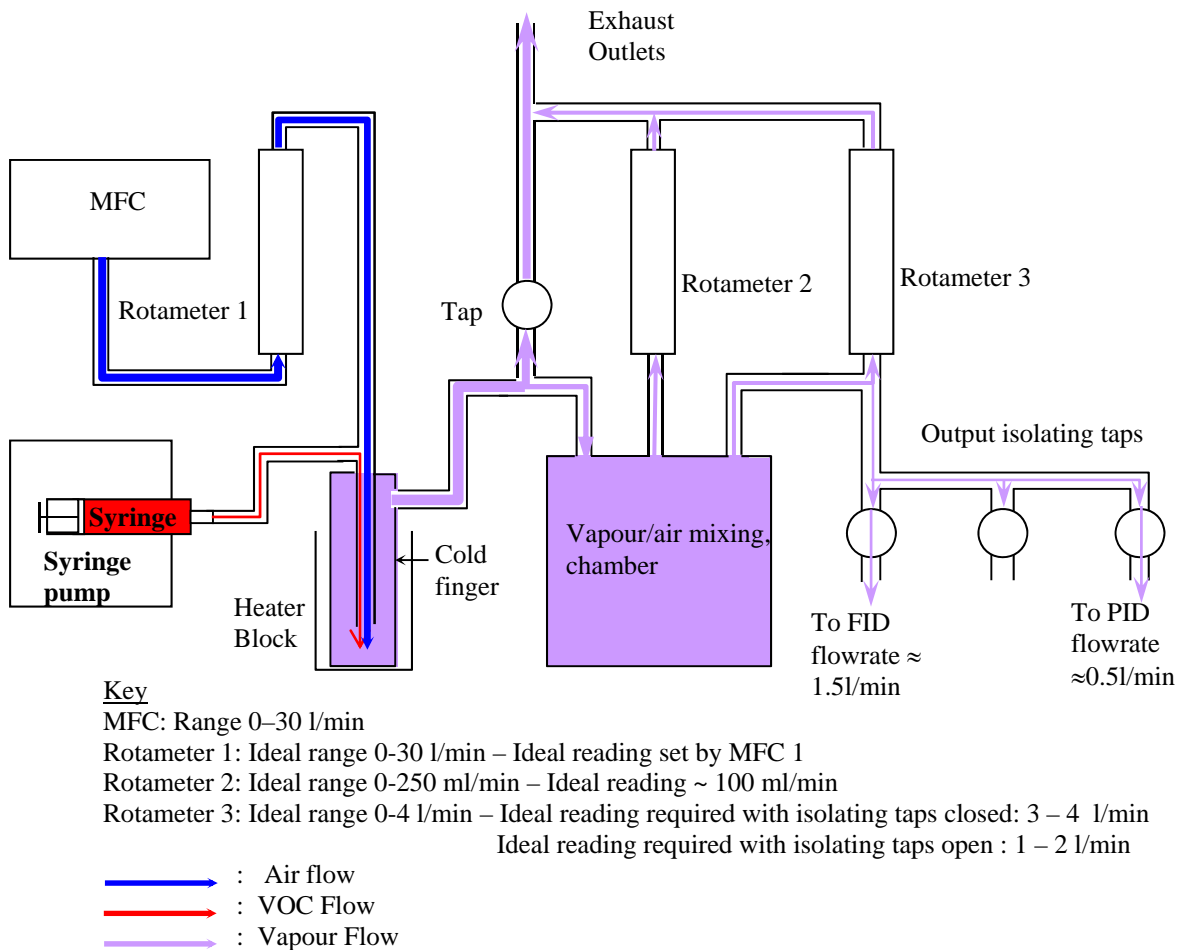


Figure 3.1: Schematic diagram of the dynamic vapour production system

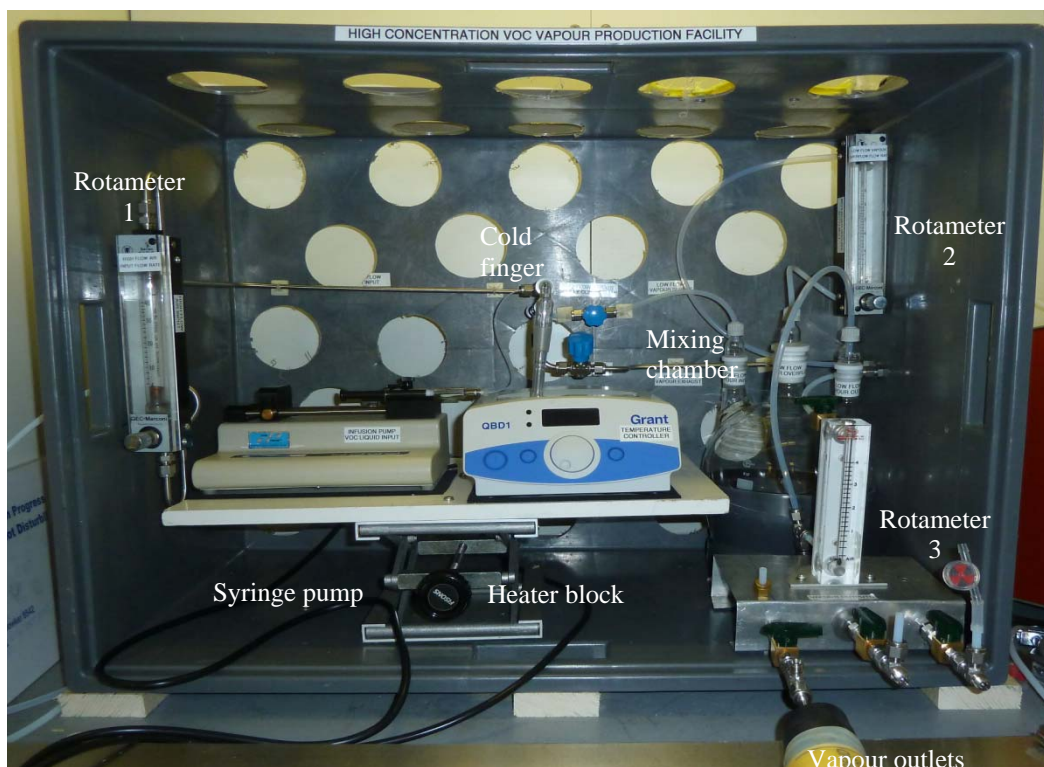


Figure 3.2: Photograph of the dynamic vapour production system

The heater block and therefore the air inside the evaporation chamber (cold finger) is set to a pre-determined temperature. The syringe pump introduces the liquid VOC at a pre-determined flow rate into the evaporation chamber via 0.5 m of 20 gauge FEP tubing as a fine spray. The air is simultaneously fed into the evaporation chamber at a pre-determined flow rate via the mass flow controller (MFC) causing the VOC to vaporize inside the evaporation chamber.

Experience in using a similar set up at HSL suggests an optimum chamber temperature, air flow rate and VOC injection rate should effect maximum vaporization. This air flow rate is much higher than the combined flow rates required by the FID and the instruments to be calibrated at the outputs. Therefore, as the vapour flows from the evaporation chamber at the high flow rate, the excess is exhausted into the fume cupboard via a controlling tap, before it enters the mixing/expansion chamber at a flow rate around 2 l/min greater than the combined flow rates of the FID and the instruments to be calibrated. This greater flow into the mixing chamber allows for fluctuations in the flow rates of the FID (flow rate ~ 1.5 l/min) and the instruments to be calibrated, the excess is exhausted from the chamber into the fume cupboard and monitored on rotameter 2.

The mixing chamber allows the vapour to mix thoroughly and damps the effect of the stepper motor in the syringe pump, creating a more homogenous, even and settled concentration. The vapour then flows to the 3 outlet isolating taps and rotameter 3 (which acts as a Y tube for all 3 outlets), a positive reading on which shows that there is a positive pressure and therefore excess flow at the outlets when the instruments are connected.

For the system to be operating properly all of the rotameters must be displaying positive flow rates when the FID and the instrument(s) to be calibrated are connected and operating. Any outlet to which no instrument is connected should be closed using the isolating taps to prevent the possibility of air entering into the system or vapour leaving the system via that route.

Tests were performed over various heater block (evaporation chamber) temperatures, VOC injection rates and air flow rates, the ranges of which were selected from experience of using a similar set up available at HSL. These ranges are shown in Table 3.2.

Table 3.2: Evaporation chamber temperature range, VOC injection rate range and air flow rate range investigated

| VOC | Evaporation chamber temperature range (°C) | VOC injection rate range (ml/hr) | Air flow rate range (l/min) |
|---------|--|----------------------------------|-----------------------------|
| Toluene | 60 – 90* | 1 – 15 ml/hr | 17.5 – 22.5 |
| Xylene | 60 – 100* | 1 – 15 ml/hr | 17.5 – 22.5 |

***Ranges limited to safe values below the relative boiling points**

The concentration of the VOC in the vapour generated was detected using a FID which had previously been calibrated to certified concentrations of the VOC under investigation and connected to one of the outlet isolating taps, the other 2 outlet isolating taps being closed. The sampling tube of the FID is maintained at a temperature higher than the ambient temperature to maintain the VOC in the vapour phase until it reaches the FID analyser. The tests were performed until liquid droplets could be seen on the inside of the evaporation chamber, signifying that complete vaporization was no longer occurring.

Further tests were performed to investigate the consistency of the generated concentrations. As the FID has no internal data logging facility, a computer program was written in Lab View to log the data readings from the FID. This allowed the consistency of the output concentration to be observed and compared with that detected from similar vapour concentrations supplied commercially in cylinders.

3.3 RESULTS

The concentration (C) of VOC vaporized in the system at a VOC injection rate (V) and air flow rate (A) at an ambient temperature of 20 °C and pressure of 1 bar (assuming complete vaporization) can be estimated by Equation 3.1.

$$C \text{ (ppm)} = \{V \text{ (ml/min)} \times \text{density (mg/ml)} / A \text{ (m}^3\text{/min)}\} \times \{24.45 / \text{Molecular wt}\} \quad \text{Equ 3.1}$$

These values were only used as general guidelines as the temperature of the system is much higher than room temperature at which the values in the predictive equations are given.

Initial tests into the temperature of the evaporation chamber showed that the maximum safe temperature would be optimum for vapour production.

The following tests using toluene and xylene were therefore performed with the temperature of the evaporation chamber set to 90 °C and 100°C respectively.

3.3.1 Toluene concentrations generated

The concentrations of toluene detected by the FID at the various settings along with the estimated values are shown in Figures 3.3 and 3.4 and summarised in Table 3.3.

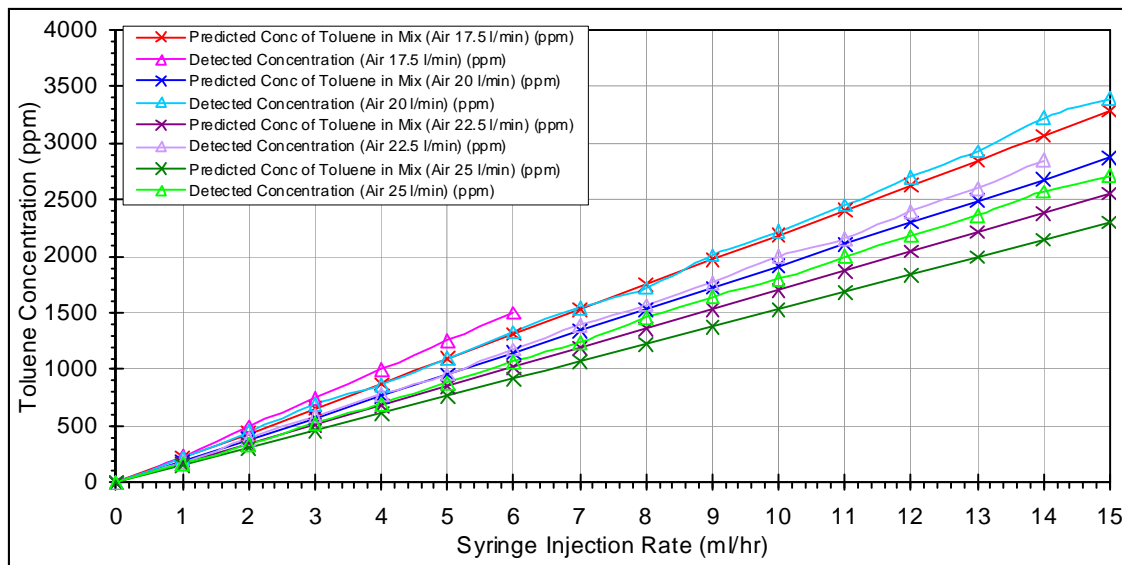


Figure 3.3: Predicted and detected concentrations of toluene over the range of air flow as a function of syringe injection rate

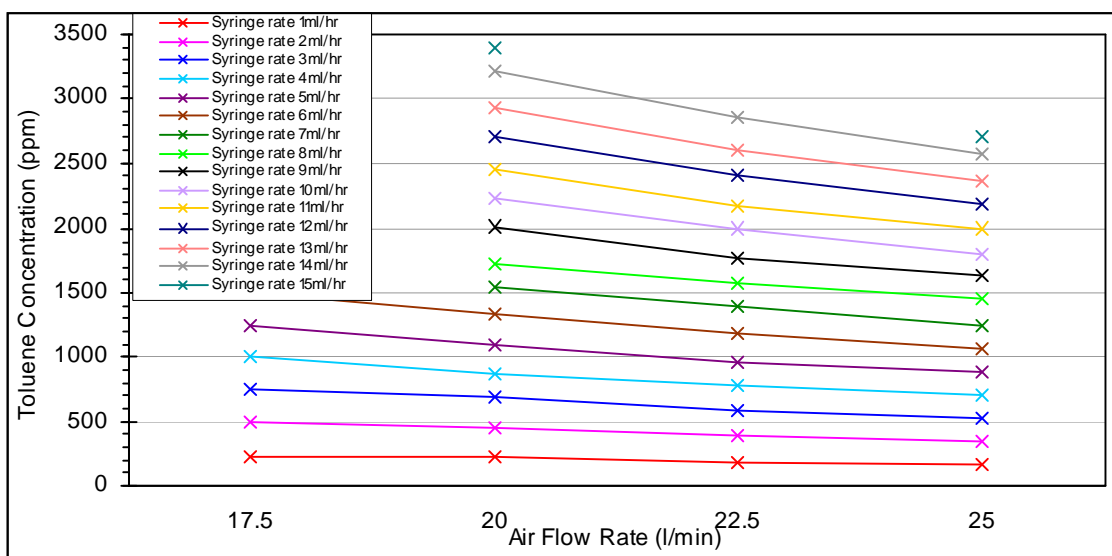


Figure 3.4: Detected concentrations of toluene over the range of syringe injection rate as a function of air flow

Table 3.3: Predicted and estimated concentrations of toluene

| Syringe injection rate (ml/hr) | Toluene concentration in vapour mix (ppm) | | | | | | | |
|--------------------------------|---|--------------|---------------------|----------|-----------------------|--------------|---------------------|----------|
| | (Air F/R: 17.5 l/min) | | (Air F/R: 20 l/min) | | (Air F/R: 22.5 l/min) | | (Air F/R: 25 l/min) | |
| | Estimated | Detected | Estimated | Detected | Estimated | Detected | Estimated | Detected |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 219 | 230 | 192 | 220 | 170 | 180 | 153 | 170 |
| 2 | 438 | 500 | 383 | 450 | 340 | 390 | 306 | 340 |
| 3 | 657 | 750 | 575 | 690 | 511 | 590 | 460 | 530 |
| 4 | 876 | 1000 | 766 | 870 | 681 | 785 | 613 | 700 |
| 5 | 1094 | 1260 | 958 | 1100 | 851 | 960 | 766 | 885 |
| 6 | 1313 | 1500 | 1149 | 1330 | 1021 | 1180 | 919 | 1070 |
| 7 | 1532 | inconsistent | 1341 | 1550 | 1192 | 1390 | 1073 | 1240 |
| 8 | 1751 | inconsistent | 1532 | 1720 | 1362 | 1570 | 1226 | 1460 |
| 9 | 1970 | inconsistent | 1724 | 2010 | 1532 | 1770 | 1379 | 1640 |
| 10 | 2189 | inconsistent | 1915 | 2220 | 1702 | 2000 | 1532 | 1800 |
| 11 | 2408 | inconsistent | 2107 | 2450 | 1873 | 2160 | 1685 | 2000 |
| 12 | 2627 | inconsistent | 2298 | 2700 | 2043 | 2400 | 1839 | 2180 |
| 13 | 2845 | inconsistent | 2490 | 2930 | 2213 | 2600 | 1992 | 2360 |
| 14 | 3064 | inconsistent | 2681 | 3220 | 2383 | 2850 | 2145 | 2570 |
| 15 | 3283 | inconsistent | 2873 | *3390 | 2554 | inconsistent | 2298 | *2710 |

*inconsistent but can be estimated

The concentrations of toluene detected by the FID over the ranges of air flow rates and syringe injection rates in Figures 3.3 and 3.4 show the concentrations tend to increase linearly as the syringe injection rate increases but increase linearly as the air flow rate decreases to the point where total evaporation ceases to occur and liquid droplets were beginning to form on the inside of the evaporation chamber.

The highest concentration of toluene vapour achieved (whilst still maintaining total evaporation) of ~ 3220 ppm occurred when the air flow rate was set to 20 l/min and the syringe injection rate was set to 14 ml/min. Concentrations greater than this were discounted as liquid droplets were

beginning to form on the inside of the evaporation chamber and the concentration reading was becoming very inconsistent, however, where readings could be estimated despite this inconsistency they are included in Figures 3.3 and 3.4 and Table 3.3 for information. Therefore concentrations approaching the lower flammability limit could not be achieved.

3.3.2 Xylene concentrations generated

The concentrations of xylene detected by the FID at the various settings along with the estimated values are shown in Figures 3.5 and 3.6 and summarised in Table 3.4.

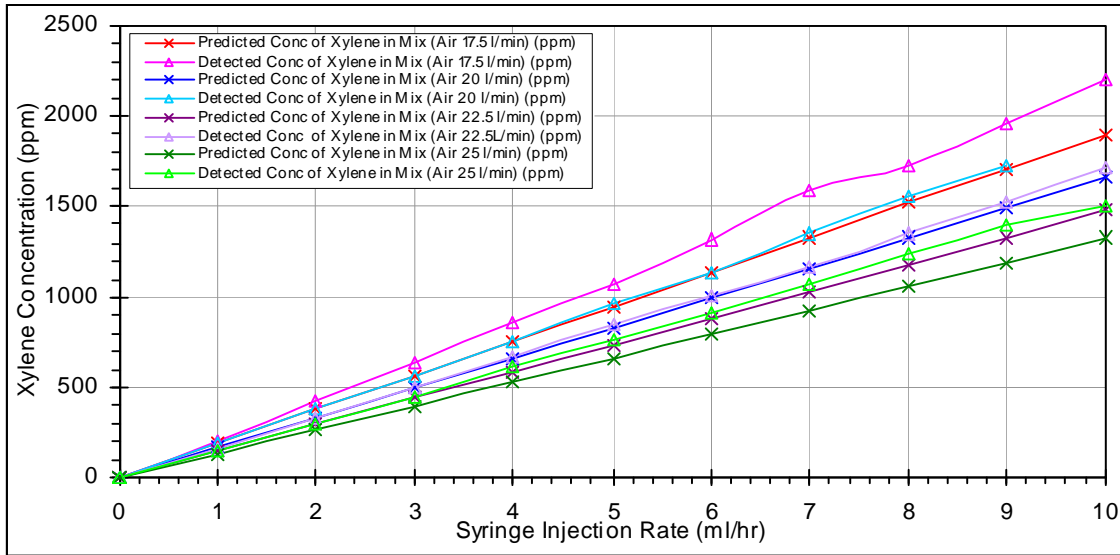


Figure 3.5: Predicted and detected concentrations of xylene over the range of air flow as a function of syringe injection rate

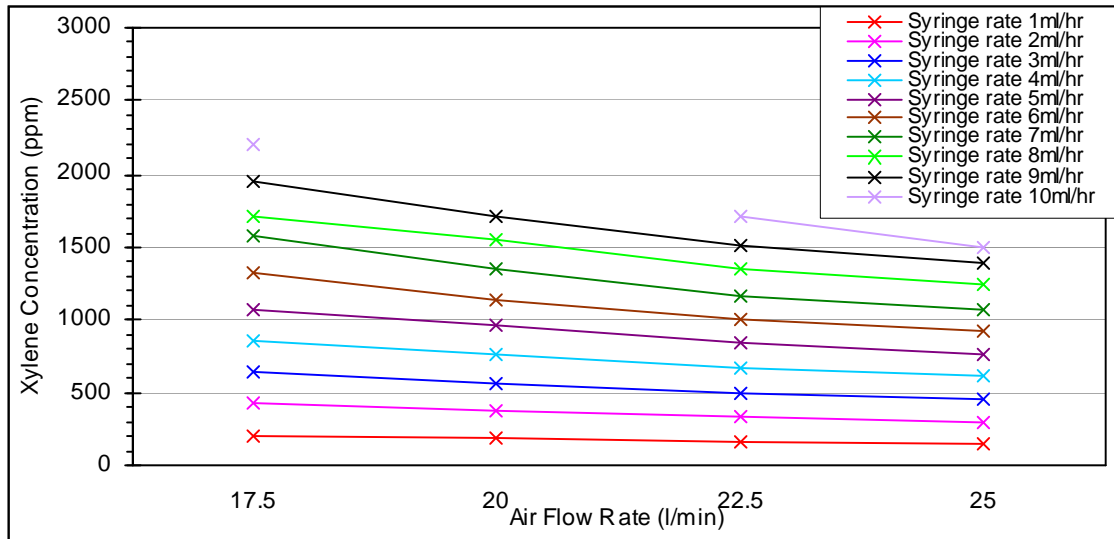


Figure 3.6: Detected concentrations of xylene over the range of syringe injection rate as a function of air flow

Table 3.4: Predicted and estimated concentrations of xylene

| Syringe rate (ml/hr) | Xylene concentration in vapour mix (ppm) | | | | | | | |
|----------------------|--|----------|---------------------|--------------|-----------------------|----------|---------------------|----------|
| | (Air F/R: 17.5 l/min) | | (Air F/R: 20 l/min) | | (Air F/R: 22.5 l/min) | | (Air F/R: 25 l/min) | |
| | Estimated | Detected | Estimated | Detected | Estimated | Detected | Estimated | Detected |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 190 | 205 | 166 | 190 | 148 | 160 | 133 | 150 |
| 2 | 379 | 430 | 332 | 380 | 295 | 330 | 266 | 300 |
| 3 | 569 | 640 | 498 | 560 | 443 | 500 | 398 | 450 |
| 4 | 759 | 860 | 664 | 760 | 590 | 670 | 531 | 620 |
| 5 | 948 | 1071 | 830 | 970 | 738 | 850 | 664 | 770 |
| 6 | 1138 | 1320 | 996 | 1140 | 885 | 1010 | 797 | 920 |
| 7 | 1328 | 1580 | 1162 | 1350 | 1033 | 1170 | 929 | 1070 |
| 8 | 1517 | 1720 | 1328 | 1550 | 1180 | 1350 | 1062 | 1240 |
| 9 | 1707 | *1960 | 1494 | *1720 | 1328 | 1520 | 1195 | 1390 |
| 10 | 1897 | *2200 | 1660 | inconsistent | 1475 | *1710 | 1328 | *1500 |

*inconsistent but can be estimated

The concentrations of xylene detected by the FID over the ranges of air flow rates and syringe injection rates in Figures 3.5 and 3.6 again show the concentrations tend to increase linearly as the syringe injection rate increases, but increase linearly as the air flow rate decreases to the point where total evaporation ceases to occur and liquid droplets were beginning to form on the inside of the evaporation chamber.

The highest concentration of xylene vapour achieved (whilst still maintaining total evaporation) of ~ 1720 ppm occurred when the air flow rate was set to 17.5 l/min and the syringe injection rate was set to 8 ml/min. Concentrations greater than this were discounted as liquid droplets were beginning to form on the inside of the evaporation chamber and the concentration reading was becoming very inconsistent, however, where readings could be estimated despite this inconsistency they are included in Figures 3.5 and 3.6 and Table 3.4 for information. Therefore, as with toluene, concentrations approaching the lower flammability limit could not be achieved.

3.3.3 Calibration of generator to toluene and xylene

Figure 3.7 shows the detected concentrations of toluene and xylene at the optimum air flow rates of 20 l/min and 17.5 l/min respectively as functions of syringe injection rates, and the equations of the trend lines show the relationships between the actual VOC concentrations and the syringe pump settings

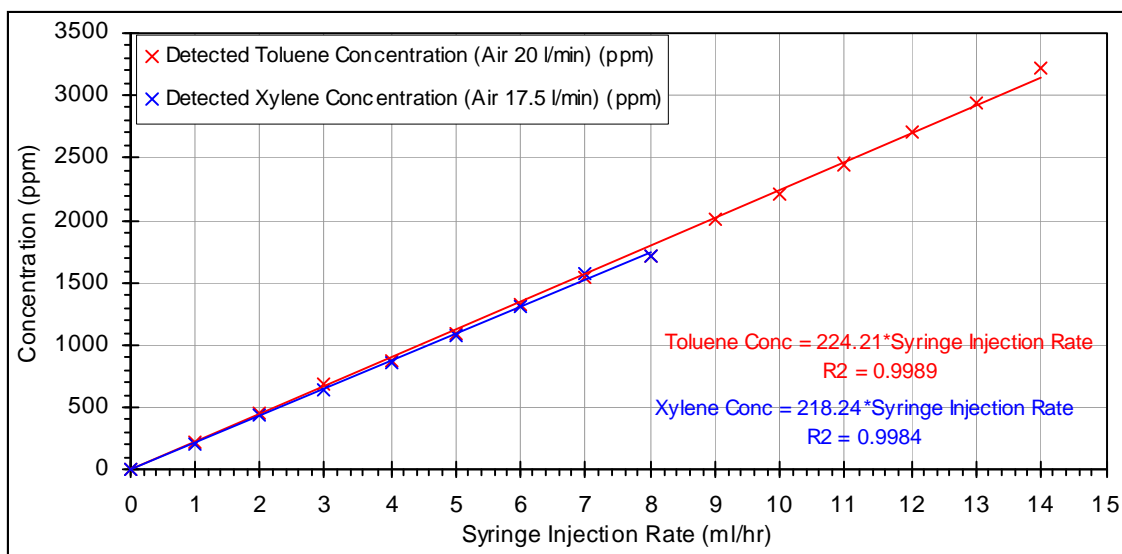


Figure 3.7: Detected concentrations of toluene and xylene at optimum air flow rates

For toluene vaporization, if the temperature of the evaporation chamber and the air flow rate are maintained at 90 °C and 20 l/min respectively then the relationship between the syringe pump setting and the actual toluene concentration is given by Equation 3.2

$$\text{Toluene Concentration} = 224.21 \times \text{Syringe Injection Rate} \quad \text{Equ 3.2}$$

For xylene vaporization, if the temperature of the evaporation chamber and the air flow rate are maintained at 100 °C and 17.5 l/min respectively then the relationship between the syringe pump setting and the actual xylene concentration is given by Equation 3.3

$$\text{Xylene Concentration} = 218.24 \times \text{Syringe Injection Rate} \quad \text{Equ 3.3}$$

3.4 VARIABILITY OF THE GENERATED VAPOUR CONCENTRATION

3.4.1 Methodology

The FID was calibrated to 794 ppm of toluene supplied from a cylinder and then exposed to similar concentrations of toluene supplied from the generator and from certified cylinders. The FID was then calibrated to 653 ppm of xylene supplied from a cylinder and exposed to similar concentrations of xylene supplied from the generator and from certified cylinders. The variability of the concentrations detected for each situation was compared over a measurement period of approximately 10 minutes.

3.4.2 Results

The average, actual standard deviations and relative standard deviations of concentrations of toluene and xylene detected over the exposure period at concentrations supplied from the generator and from cylinders are shown in Table 3.5 (see Appendix 3, Section 8.3 for data in graphical form).

Table 3.5: Average, actual and relative standard deviations of concentrations of toluene and xylene detected at various concentrations supplied from the generator and from cylinders

| Toluene Supply Method | Ave FID Reading (ppm) | SD (ppm) [*Rel SD%] | Xylene Supply Method | Ave FID Reading (ppm) | SD (ppm) [*Rel SD%] |
|------------------------------|------------------------------|----------------------------|-----------------------------|------------------------------|----------------------------|
| Cylinder | 376 | 0.6 [0.2] | Generator | 158 | 1.9 [1.2] |
| Generator | 386 | 7.1 [1.8] | Generator | 315 | 3.7 [1.2] |
| Cylinder | 593 | 1.2 [0.2] | Cylinder | 372 | 1.2 [0.3] |
| Generator | 584 | 8.2 [1.4] | Generator | 479 | 3.7 [0.8] |
| Cylinder | 797 | 1.2 [0.2] | Generator | 645 | 4.6 [0.7] |
| Generator | 787 | 9.9 [1.3] | Cylinder | 767 | 2.1 [0.3] |
| Cylinder | 2071 | 5.3 [0.3] | Generator | 806 | 5.4 [0.7] |
| Generator | 2233 | 22.4 [1.0] | Generator | 970 | 6.2 [0.6] |
| Cylinder | 3085 | 6.1 (0.2) | | | |
| Generator | 3146 | 36.2 (1.2) | | | |

*Percentage of the average reading

When either of the vapours is supplied via the generator or the cylinders, the actual standard deviations of the detected concentrations about the average increase with increase in concentration. However, if these values are taken as relative values (percentages of the actual detected concentrations), for a given vapour, using a given method of supply, they are independent of, and comparable at, all concentrations.

For toluene:

- When the vapour is supplied from cylinders the relative standard deviations of the results range from 0.2% to 0.3% (ave: 0.2%) of the average concentrations.
- When the vapour is supplied from the generator the relative standard deviations of the results range from 1.0% to 1.8% (ave: 1.3%) of the average concentrations.

For xylene:

- When the vapour is supplied from cylinders the relative standard deviations of the results is 0.3% of the average concentrations.
- When the vapour is supplied from the generator the relative standard deviations of the results range from 0.6% to 1.2% (ave: 0.9%) of the average concentrations.

In both cases the variability of the concentrations supplied from the cylinders is less than that using similar concentrations supplied from the generator. The variation from the cylinder supply is due to the measuring instrument, while that of the generator is due to the generation method and the instrument.

However, a worst case standard deviation of 1.8% of the average reading is much better than the documented accuracy of most monitors of $\pm 10\%$.

4. TESTING OF PIDS AT HIGHER GENERATED CONCENTRATIONS

4.1 GENERAL

The most suitable vapour generation system was found to be the dynamic system and this was therefore used to investigate the accuracy of a commonly used PID based instrument at concentrations greater than those available commercially in cylinders. As the maximum concentration of toluene generated by the system was not significantly greater than that available commercially, this part of the investigation was only performed using xylene.

The variability of the concentrations detected by the PID at similar concentrations of toluene and xylene supplied from the generator and from certified cylinders were also investigated.

4.2 ACCURACY OF PIDS AT HIGHER CONCENTRATIONS

4.2.1 Methodology

The FID and PID were calibrated to 653 ppm of xylene supplied from a cylinder and exposed simultaneously to concentrations of xylene generated by the system set to the optimum conditions determined in Section 3 of this report. The concentrations detected by the PID were compared to those detected by the FID.

4.2.2 Results

The concentrations of xylene detected by the PID at settings confirmed by the FID are shown in Table 4.1 and Figure 4.1

Table 4.1: Xylene vapour detected by the FID and PID at various concentrations supplied from the vapour generator up to the system saturation point

| FID detected concentration (ppm) | PID detected concentration (ppm) | Error in detected PID concentration (%) |
|----------------------------------|----------------------------------|---|
| 0 | 0 | 0 |
| 205 | 210 | 2 |
| 430 | 430 | 0 |
| 640 | 650 | 2 |
| 860 | 870 | 1 |
| 1071 | 1080 | 1 |
| 1320 | 1300 | -2 |
| 1580 | 1450 | -8 |
| 1720 | 1580 | -8 |
| 1960 | 1800 | -8 |
| 2200 | 2030 | -8 |

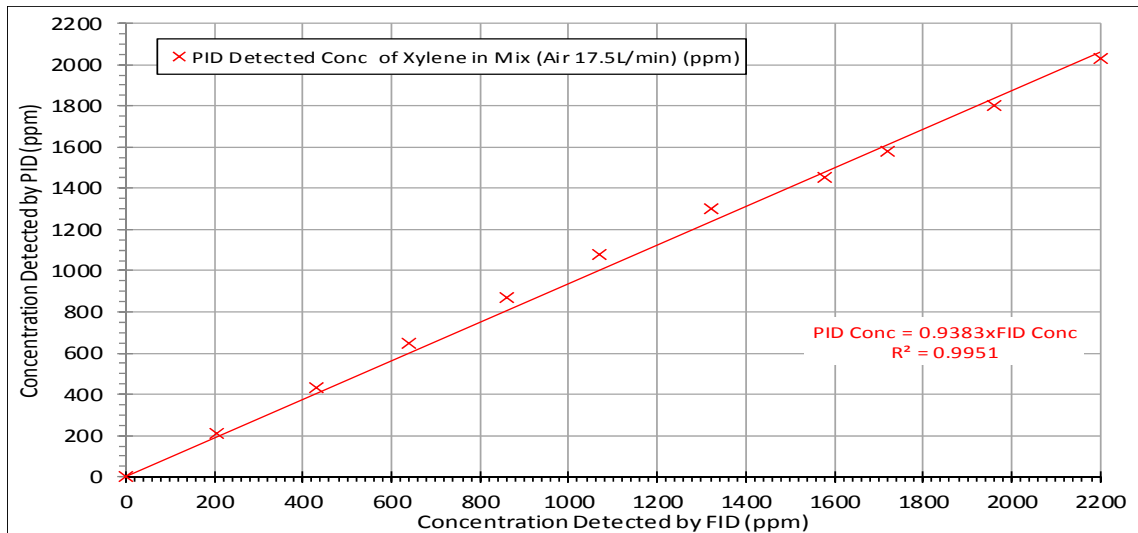


Figure 4.1: Xylene vapour detected by the FID and PID at various concentrations supplied from the vapour generator up to the system saturation point

The concentrations of xylene vapour detected by the PID are comparable (within 1%) to those detected by the FID over the full range from 0 to 2200 ppm and well within the documented accuracy specifications of the PID of $\pm 10\%$.

4.3 VARIABILITY OF CONCENTRATIONS DETECTED BY PIDS

4.3.1 Methodology

The PID was calibrated to 794 ppm of toluene supplied from a cylinder and then exposed to similar concentrations of toluene supplied from the generator and from certified cylinders. The PID-based instrument was then calibrated to 653 ppm of xylene supplied from a cylinder and then exposed to similar concentrations of xylene supplied from the generator and from certified cylinders. This was performed as part of the procedure in Section 3.4, and the variability of the concentrations detected were compared over a similar period.

4.3.2 Results

The average, actual standard deviations and relative standard deviations of concentrations of toluene and xylene detected by the PID-based instrument over the exposure period at concentrations supplied from the generator and from cylinders are shown in Table 4.2 (see Appendix 3, Section 8.3 for data in graphical form).

Table 4.2: Average, standard deviations and relative standard deviations of concentrations of toluene and xylene detected by the PID based instrument at various concentrations supplied from the generator and from cylinders

| Toluene Supply Method | Ave PID Reading (ppm) | SD (ppm) [*Rel SD%] | Xylene Supply Method | Ave PID Reading (ppm) | SD (ppm) [*Rel SD%] |
|------------------------------|------------------------------|----------------------------|-----------------------------|------------------------------|----------------------------|
| Cylinder | 381 | 2.8 [0.7] | Generator | 170 | 1.9 [1.1] |
| Generator | 384 | 6.6 [1.7] | Generator | 323 | 3.3 [1.0] |
| Cylinder | 570 | 1.5 [0.3] | Cylinder | 373 | 0.5 [0.1] |
| Generator | 561 | 8.3 [1.5] | Generator | 465 | 3.7 [0.8] |
| Cylinder | 766 | 2.8 [0.4] | Generator | 626 | 5.0 [0.8] |
| Generator | 759 | 11.3 [1.5] | Cylinder | 762 | 2.8 [0.4] |
| Cylinder | 1877 | 14.9 [0.8] | Generator | 769 | 6.0 [0.8] |
| Generator | 1951 | 17.3 [0.9] | Generator | 896 | 6.1 [0.7] |

*Percentage of the average reading

When either of the vapours is supplied via the generator or the cylinders, the actual standard deviations of the detected concentrations about the average increase with increase in concentration. However, if these values are taken as relative values (percentages of the actual detected concentrations), for a given vapour, using a given method of supply, they are independent of, and comparable at, all concentrations.

For toluene:

- When the vapour is supplied from cylinders the relative standard deviations of the results range from 0.3% to 0.8% (ave: 0.6%) of the average concentrations.
- When the vapour is supplied from the generator the relative standard deviations of the results range from 0.9% to 1.7% (ave: 1.4%) of the average concentrations

For xylene:

- When the vapour is supplied from cylinders the relative standard deviations of the results range from 0.1% to 0.4% (ave: 0.3%) of the average concentrations.
- When the vapour is supplied from the generator the relative standard deviations of the results range from 0.7% to 1.1% (ave: 0.9%) of the average concentrations

The variability of the concentrations of the VOC vapour detected by the PID monitor when the vapour is supplied via the generator or the cylinders is comparable to that of the more accurate FID monitor and is well within the documented accuracy of the PID monitor of $\pm 10\%$.

5. CONCLUSIONS

The static system of VOC vapour production for generating concentrations of VOCs higher than those available commercially in cylinders was unsuccessful. This is due to the fact that the concentration of the VOC vapour cannot be easily controlled, and the effect of the concentration produced on the operation of the monitors is uncertain.

The dynamic system of VOC vapour production for generating concentrations of VOCs higher than those available commercially in cylinders was, however, moderately successful, producing calibrated, repeatable, higher vapour concentrations of toluene and xylene than those available commercially in cylinders which will allow the investigation of the operational characteristics of a PID monitor to concentrations up to the saturation limit of the generation system.

The maximum concentration of xylene vapour generated by the dynamic system was 1720 ppm which is 115% greater than the maximum concentration of 800 ppm available commercially in cylinders, but still only 20% of the maximum predicted concentrations of 8,700 ppm at an ambient temperature of 20 °C and pressure of 1 bar.

The maximum concentration of toluene vapour generated by the dynamic system was 3220 ppm, which is 7% greater than the maximum concentration of 3,000 ppm available commercially in cylinders, but still only 11% of the maximum predicted concentrations of 29,000 ppm at an ambient temperature of 20 °C and pressure of 1 bar.

Therefore the dynamic method of vapour generation has increased the range of xylene vapour concentrations available by more than 100%. It did not, however, significantly increase the range of toluene vapour concentrations.

It is not clear from this investigation why there is such a difference in the achievable concentration of the two vapours. The maximum concentration of VOCs available commercially in cylinders is dependent on the vapour pressure of the respective VOCs which limits the maximum pressure of the VOC in the cylinder and therefore the maximum concentrations available. Also there may be quality control/production factors to be considered. The maximum concentrations of xylene (vapour pressure: 0.0087 bar) of ~800 ppm and toluene (vapour pressure: 0.029 bar) of ~3,000 ppm available commercially in the cylinders used in this investigation, both pressurised to around 4 bar reflect the dependence of concentration on vapour pressure. However, the system described here is not pressurised. Further investigations using other VOCs may determine a relationship between the maximum possible concentration and the vapour pressure of the respective VOCs.

The output of the dynamic vapour generation system has been shown to be linear and repeatable for toluene and xylene. This should allow the system to be calibrated to a concentration available in cylinders and the generated output to be accurate at concentrations up to saturation. The levels of the generated concentrations are not as consistent as those supplied by cylinders but are well within the accuracy tolerance of most commercially available the instruments. Maintaining the temperature of the evaporation chamber and air flow rate to optimum values, the vapour concentration can be controlled from zero to the evaporation limit by adjusting the syringe injection rate.

The worst case relative variability in any given detected concentration of 1.4% of the average concentration suggests that this method of vapour generation will be of a satisfactory level of consistency.

The concentrations of the vapours at which the operational characteristics of the monitors would be affected could not be determined as the maximum possible generated concentration (saturation) was reached before any such effect was evident.

VOC concentrations approaching the lower flammability limit could not be achieved because liquid droplets formed on the inside of the evaporation chamber, resulting in inconsistent concentration readings.

The system produced in this investigation has the following advantages and disadvantages when compared to existing methods of vapour supply:

- Gas bottles: Concentration certified, more accurate and more consistent, but not as cost effective or flexible as the new system
- Existing HSL syringe pump system: Concentration does not have range or consistency of the new system
- Bubbler systems: Safety concerns due to lack of control and high probability of concentrations around LEL being produced

None of the above existing systems can provide such a wide range of accurate and cost effective VOC concentrations as the new system. The new vapour generation system allows the monitors to be calibrated to the VOCs under investigation at or around the levels expected to be encountered, and removes the problem of application of correction factors which are often inaccurate.

The dynamic vapour generation system was used to investigate the operational characteristics of a PID monitor at the higher concentrations of xylene achievable. The concentrations detected by the PID were found to be within 1 % of the actual generated concentration monitored using the more accurate FID. The variability of each of the concentrations of both toluene and xylene detected by the PID was comparable to that of the FID at those concentrations. The dynamic vapour generation system should therefore allow the investigation of the operational characteristics of a PID monitor at concentrations up to the limit of the generation system.

6. FURTHER WORK

It would be a significant improvement in the operation of the generator if the consistency of the output concentration could be improved. Further investigations into the components (eg a larger mixing chamber) and settings (eg air flows through different parts of the system) may allow improvements in this aspect of the generator.

Although the generator output is repeatable once the system has been set up, it was found that any alterations to the system, even seemingly straightforward component replacement eg capillary tube via which the VOC liquid was fed into the evaporation chamber, may require recalibration and optimisation of the system to achieve the same maximum level of vapour production. Further investigation into the effect of component replacement may allow improvements in this aspect of the generator.

Further research leading to a better understanding of why the predicted maximum concentrations could not be achieved, may allow improvements in the system and an increase the levels of vapour concentration produced.

The above considerations would allow more accurate calibration of VOC monitors over wider concentration ranges, which will improve confidence in the detected readings and therefore increase the level of safety of operatives in the field.

7. REFERENCES

- [1] BS EN ISO 6144:2006 Gas analysis. Preparation of calibration gas mixtures. Static volumetric method
- [2] BS EN ISO 6145-4:2008 Gas analysis. Preparation of calibration gas mixtures using dynamic volumetric methods. Continuous syringe injection method.
- [3] HSE (2005); EH 40 / 2005 Workplace Exposure Limits.
- [4] BS EN 60079-20-1:2010. Explosive atmospheres Part 20-1: Material characteristics for gas and vapour classification— Test methods and data. *Incorporating corrigendum July 2012*
- [5] Lide, D.R. (1998-1999). CRC Handbook of chemistry and physics. 79th Edition. CRC Press,. Boston. ISBN-0-8493-0471-7
- [6] <http://webbook.nist.gov>. (last accessed Jan 2013)

8. APPENDICES

8.1 APPENDIX 1: CALCULATION OF SATURATED VAPOUR PRESSURE USING THE ANTOINE EQUATION

The Antoine equation is shown in Equation 8.1.

$$\log_{10} P = \frac{A - B}{T + C} \quad \text{Equ 8.1.}$$

where A, B and C are Antoine coefficients specific to the VOC shown in Table 8.1, T is the temperature in Kelvin and P is the saturated vapour pressure in bar.

Table 8.1: Antoine Coefficients at temperature of 20°C and atmospheric pressure of 1 bar ^[6]:

| Constant | Toluene | Xylene |
|----------|----------|----------|
| A | 4.23679 | 4.14553 |
| B | 1426.448 | 1474.403 |
| C | -45.957 | -55.377 |

The maximum concentration of the VOC under the stated conditions is the ratio of the saturated vapour pressure and the ambient air pressure, ie

$$MaxConc = \frac{P}{P_{Ambient}}$$

8.2 APPENDIX 2: LIST OF EQUIPMENT AND PURCHASE DETAILS FOR DYNAMIC SYSTEM

Table 8.2: List of equipment and purchase details

| Item | Catalogue | Page No | Part No | Quantity |
|--|------------------------------|----------------|----------------------------|-----------------|
| Syringe Mount – Single Syringe | Fisher Scientific | 1065 | PYH-985-010E | 1 |
| Syringe - 5ml | Hamilton Syringes | 31 | 81527 | 1 |
| FEP Tubing Length: 0.5m,Gauge: 20 , OD: 1.47mm, ID: 0.86mm | Hamilton Syringes | 79 | 90620 | 1 |
| Tee Connector | Hamilton Laboratory Glass | 40 | HS12/131 | 1 |
| Cold Finger | Fisher Scientific Web Site | | QCK-610L | 1 |
| Block Heater | Fisher Scientific | 668 | BLD-560-010R (QB-D1) | 1 |
| Heater Block – 16mm | Fisher Scientific | 668 | BLD-830-520X (QB-16) | 1 |
| Flow Rate Reduction Valve | In House | NA | NA | NA |
| Inlet Flask – 3L Centre Socket Size: 34/35, Side Socket Size: 24/29 | Fisher Scientific | 1080 | QFM-750-X (FR3L/5S/33P) | 1 |
| Quick Fit Adapters (Flask Inlet Bungs) - Size: 24/29 | Fisher Scientific | 1066 | QAJ-722-Q (ST53/13) | 3 |
| Sleeves – Socket Size: 24/29 | Fisher Scientific | 1068 | FB60233 | 2 |
| Adapter - Socket Size 34/35 to Cone Size 24/29 | Fisher Scientific | 1068 | FB60258 | 1 |
| Plastic Caps with Top Aperture - 13mm | Fisher Scientific | 1085 | QAK-105-E | 10 |
| Rubber Rings | Fisher Scientific | 1085 | QAK-165-Y | 10 |

8.3 APPENDIX 3: GRAPHS SHOWING VARIATION IN GENERATED CONCENTRATIONS

8.3.1 Toluene

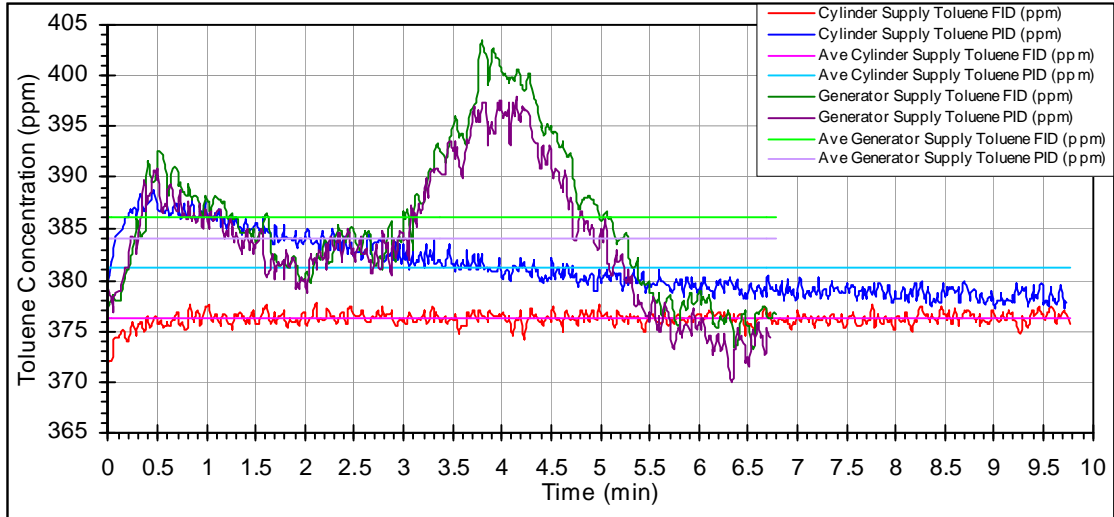


Figure 8.1: Variation in cylinder and vapour generator supply around 380 ppm toluene concentration

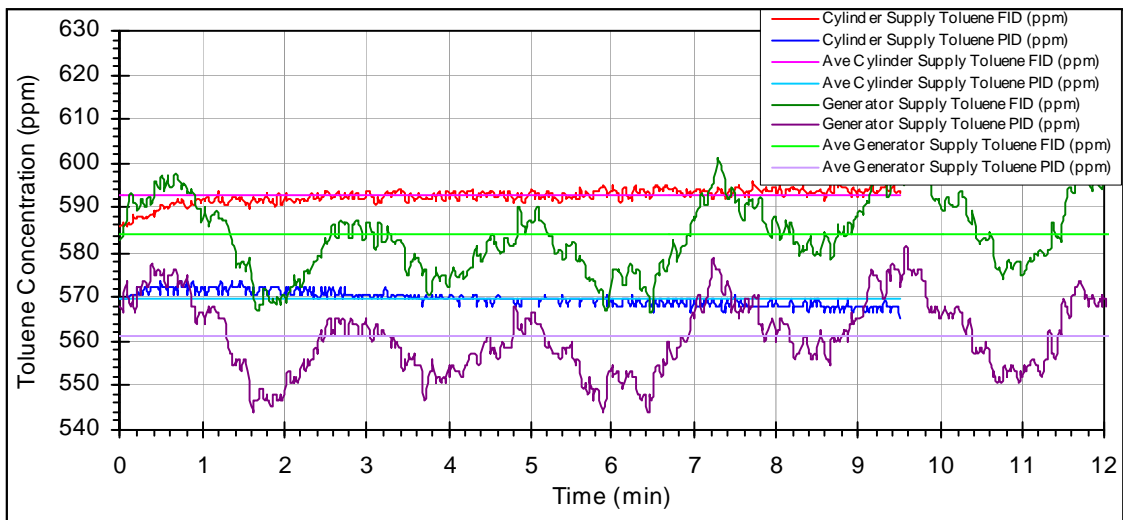


Figure 8.2: Variation in cylinder and vapour generator supply around 570 ppm toluene concentration

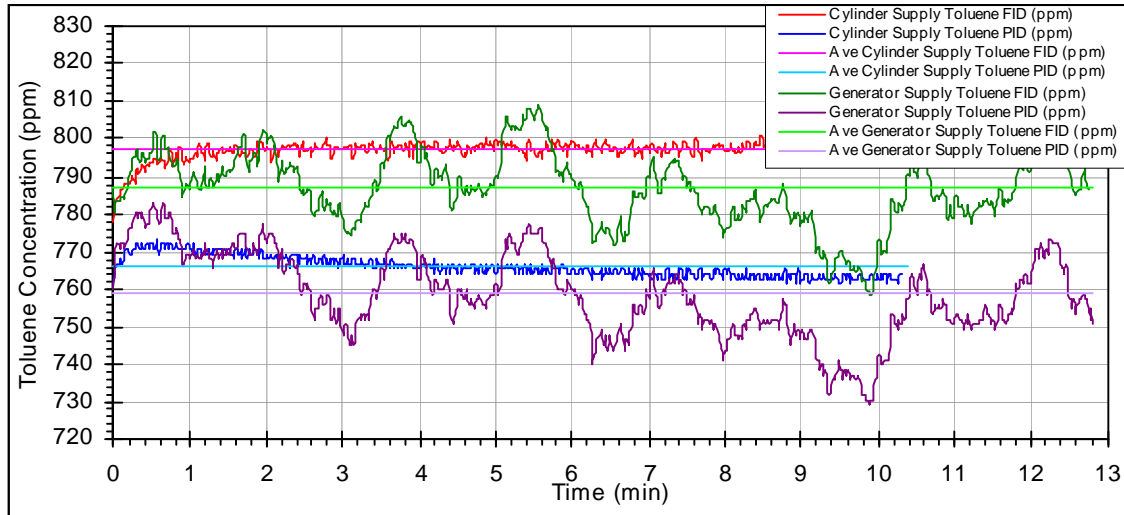


Figure 8.3: Variation in cylinder and vapour generator supply around 775 ppm toluene concentration

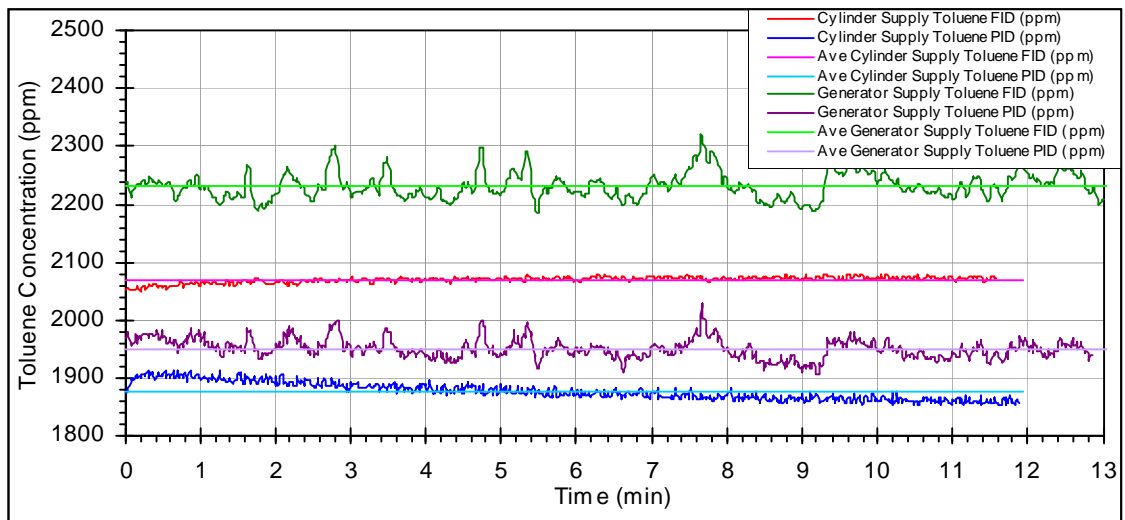


Figure 8.4: Variation in cylinder and vapour generator supply concentration around 2,000 ppm toluene concentration

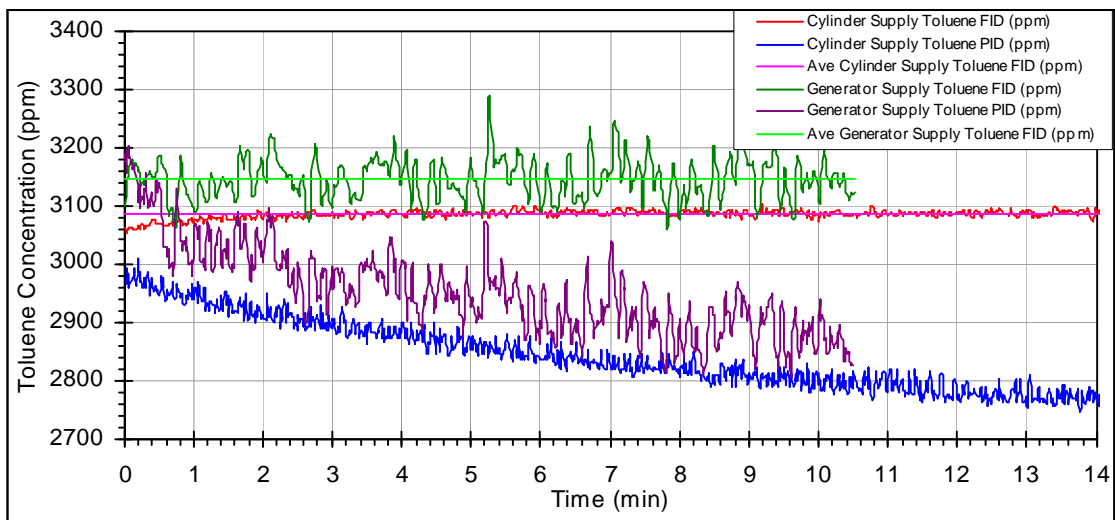


Figure 8.5: Variation in cylinder and vapour generator supply around 3,000 ppm toluene concentration

8.3.2 Xylene

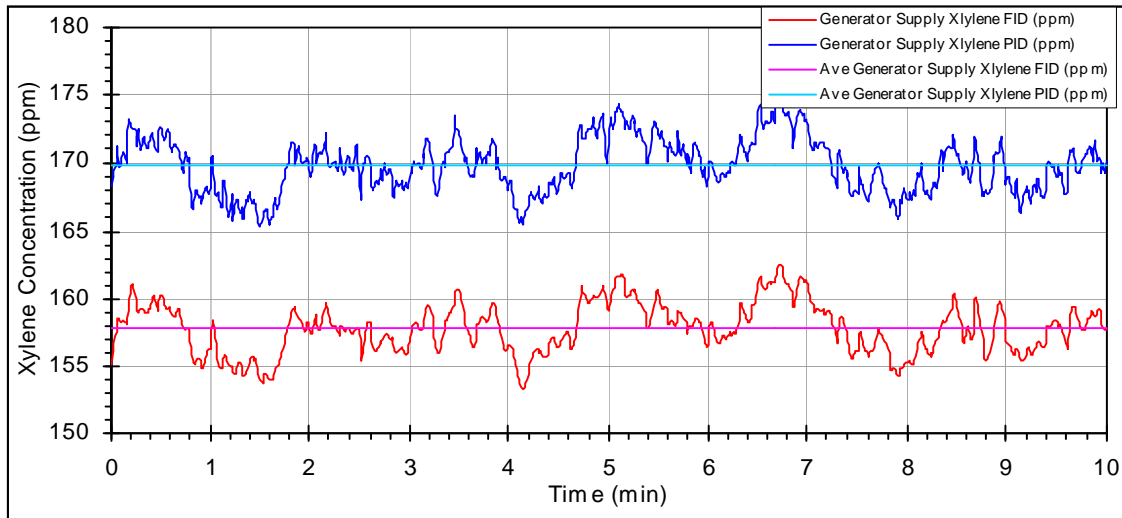


Figure 8.6: Variation in vapour generator supply around 150 ppm xylene concentration

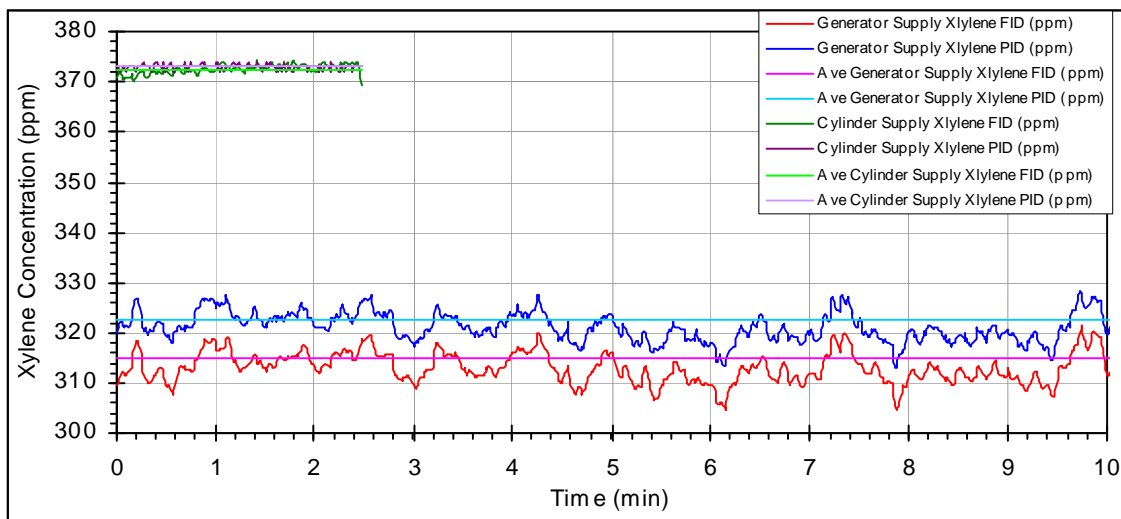


Figure 8.7: Variation in cylinder and vapour generator supply around 350 ppm xylene concentration

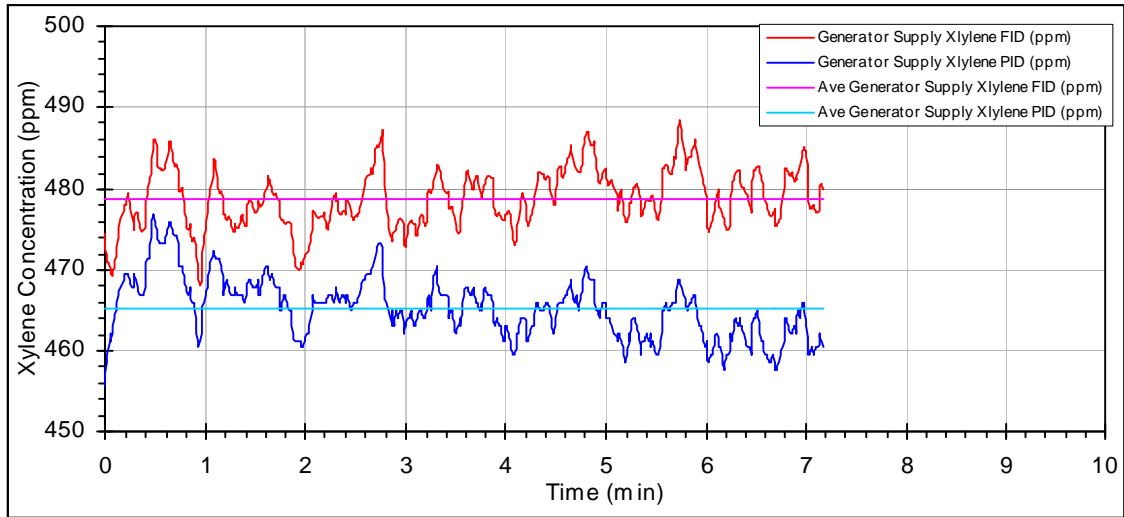


Figure 8.8: Variation in vapour generator supply around 475 ppm xylene concentration

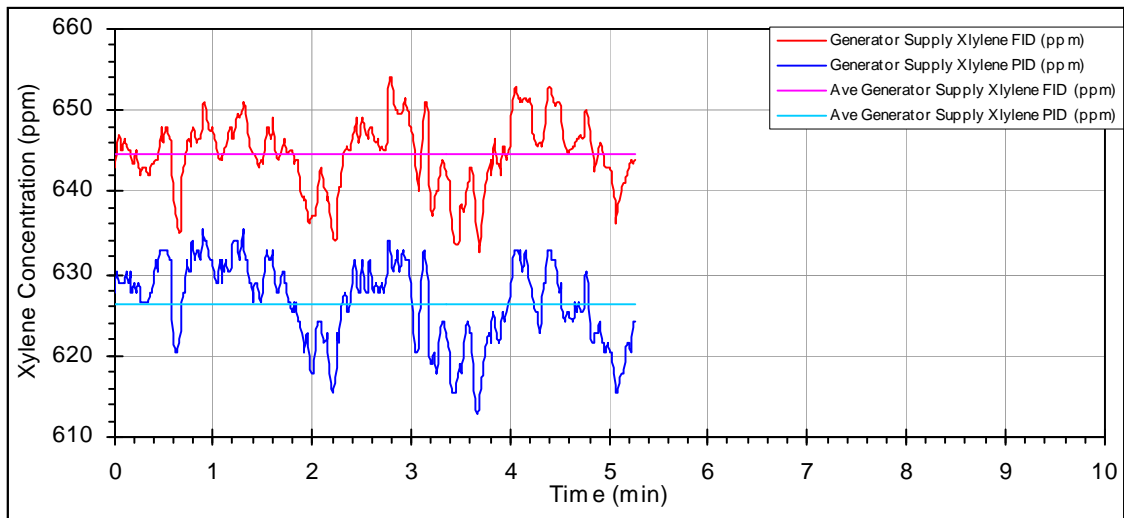


Figure 8.9: Variation in vapour generator supply around 630 ppm xylene concentration

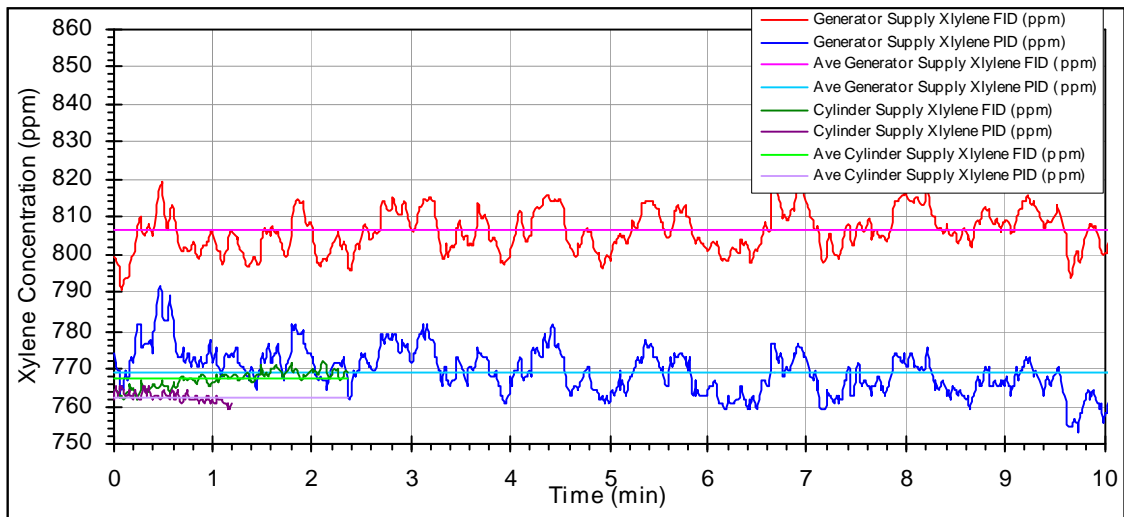


Figure 8.10: Variation in cylinder and vapour generator supply around 800 ppm xylene concentration

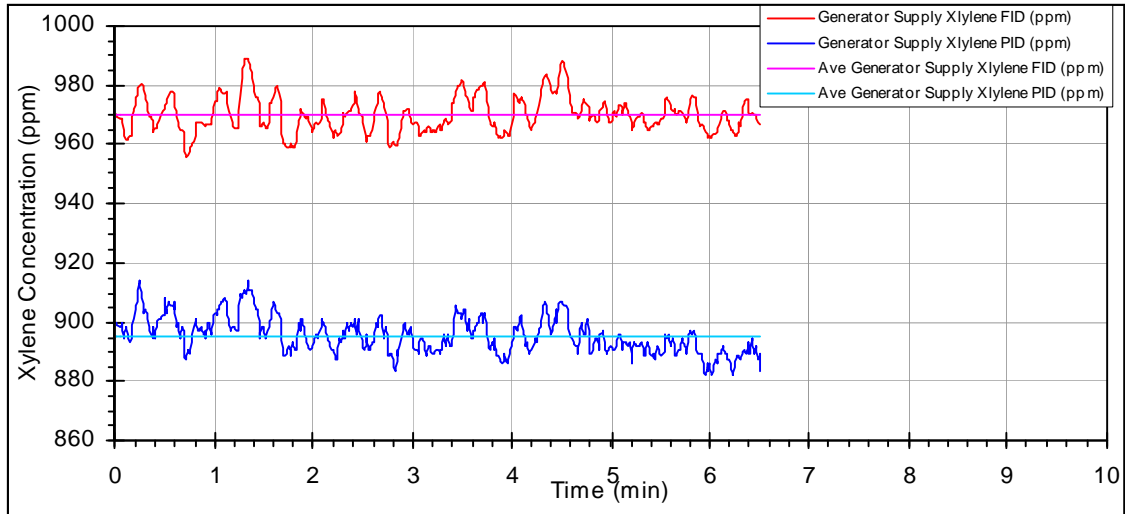


Figure 8.11: Variation in vapour generator supply around 950 ppm xylene concentration

Accuracy of photo-ionisation detectors at high concentrations of volatile organic compounds

This project was designed to develop a system which will allow the generation of vapour from selected VOC liquids at higher concentrations than can be supplied commercially in gas cylinders or from existing HSL systems, and to use this to investigate the accuracy of PIDs at these high concentrations.

Attempts to create a static system of vapour production were unsuccessful.

Attempts to create a dynamic system of vapour production were moderately successful, the maximum concentration of xylene vapour generated being 1720 ppm and the maximum concentration of toluene vapour generated being 3220 ppm. This method increased the range of xylene vapour concentrations available by more than 100%. It did not, however, significantly increase the range of toluene vapour concentrations. The output of the dynamic vapour generation system is linear and repeatable.

The accuracy of the PID at higher xylene concentrations was within 1% of the generated concentration and well within the documented instrumental tolerances of $\pm 10\%$ of the reading. The worst case relative deviation in the results of 1.4% suggests that this method of vapour generation will be of a satisfactory level of consistency to allow the investigation of the operational characteristics of a PID monitor at concentrations up to the limit of the generation system.

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