APPENDIX C QA/QC Procedures at Clyde Analytical Laboratory

METHOD ATD 1.1

THE DETERMINATION OF AMBIENT (ENVIROMENTAL) LEVELS OF BTX IN THE ATMOSPHERE USING THERMAL DESORPTION

1. INTRODUCTION AND SCOPE

BTX is the common name of a mixture of aromatic hydrocarbons containing benzene, toluene, and m- xylene. It is analysed at ambient levels in the atmosphere using a thermal desorption technique in an application range dependant on each analyte's uptake rate, overall sampling time and volume sampled. The detection limit is therefore classed as the minimum amount that can be detected on the tube and is 20ng for benzene and 40ng for toluene and m-xylene. All other volatile organic compounds present in the ambient atmosphere which are extractable onto the selected packing may be analysed qualitatively and semiquantitatively.

2. PRINCIPLE OF METHOD

BTX is absorbed from the atmosphere onto a non-volatile adsorbent known as Tenax contained in a capped tube. It is then extracted by heating the tube in a stream of inert gas and concentrating up on a low thermal mass cold trap. This trap is heated rapidly to remove the volatiles which are then swept onto a GC capillary column for subsequent analysis and identification by Mass Spectrometry.

3. REAGENTS AND APPARATUS

3.1 Tenax - TA 60-80 mesh (Perkin-Elmer cat no 0497-8064) - for tube and trap packing.
3.2 Stainless steel sample tube - fitted with end storage caps and a pen clip.
3.3 Silver coloured diffusion caps - for diffusive sampling.
3.4 Pump - for pumped sampling.
3.5 Stainless steel mesh gauzes.
3.6 Tube spring holders.
3.7 Gauze loading rig - for packing tubes.
3.8 Glass wool - handled with tongs only.
3.9 GC Injector for standard application - Injector on a Perkin-Elmer Sigma 3 GC.
3.10 Calibrated stopwatch for 2 minute standard application - EQ 258.
3.11 Calibrated 5ul syringe - checking 10ul syringe.
3.12 10ul syringe - 1ul standard application.

4. STANDARD SOLUTIONS

4.1 Calibrating standards
Four BTX standards are used in the range 20-500ng benzene and 40-1000ng toluene and m-xylene. These are based on a 1ul standard volume. Carry out the following procedures as described in table 4.1A below for standard preperation using only grade A glassware. Assign each standard with a relevant reference indicating that they are calibrating standards.

STANDARD	REQUIRED CONCENTRATION	PREPERATION
Stock Standard/Mix 1	0.5% Benzene Source 1	Take 0.5ml 99% Benzene and add to a 100ml volumetric flask using a 1ml graduated pipette.
	1% Toluene Source 1	Take 1ml 99% Toluene and add to a 100ml volumetric flask using a 1ml graduated pipette
	1% m-Xylene Source 1	Take 1ml m-xylene and add to a 100ml volumetric flask using a 1ml graduated pipette
		Add methanol to the volumetric flask and make up to 100ml.
Working Standard/Mix 2	500ng Benzene 1000ng Toluene 1000ng m-Xylene	Take 10ml stock standard and make up to 100ml with methanol using a 10ml grade A bulb pipette.
Working Standard/Mix 3	250ng Benzene 500ng Toluene 500ng m-Xylene	Take 50ml standard 2 and make up to 100ml with methanol using 2 x 25ml grade A bulb pipettes.
Working Standard/Mix 4	50ng Benzene 100ng Toluene 100ng m-Xylene	Take 20ml standard 3 and make up to 100ml with methanol using a 20ml grade A bulb pipette.
Working Standard/Mix 5	20ng Benzene 40ng Toluene 40ng m-Xylene	Take 20ml of standard 4 and make up to 50ml with methanol using a 20ml grade A bulb pipette.

Table 4.1A

During calibration, 1ul of each standard is added to the tube which then corresponds to the concentrations in ng above. Check the standard log book for the correct source of concentrated standard to be used. It will have its own unique reference.

4. STANDARD SOLUTIONS continued

4.2 Calibration check standard.
Once the calibration has been completed a calibration check comes into effect on a more routine basis where one standard in the calibrating standard range is ran as a sample with the obtained concentration being within the control and warning limits of the stored calibration. This is carried out for each day of BTX analysis and with each batch of samples. Standard mix 3 is the standard that is used for this check and it is prepared as indicated in table 4.1A.

4.3 Independant QC calibration check standard.
This standard is prepared from a different source of each analyte compared with the calibrating standards. Check the standard log book for the correct source of concentrated standard to be used. It will also have its own unique reference.The purpose therefore of using this standard is to independantly check that the calibration performed is adequate and it can be prepared at the same time as the calibration stendard or alternatively on a two week "rollover" basis with the calibration check standard to ensure independant checking can be maintained. The former procedure is normally used.
4.3.1 Prepare a stock standard of the same concentration and using the same procedure as indicated in table 4.1.A. Assign it a reference indicating that it is a QC standard.
4.3.2 Prepare a working standard of the same concentration as Mix 3 and using the same procedure as indicated in table 4.1A. This will be the standard which will be ran with each calibration. Assign it a reference indicating that it is an independant QC standard.

4.4 Standard storage
In tests performed in the laboratory it was discovered that storage at room temperature was not adequate for volatiles in methanol and that toluene and m-xylene degrade over time. Stability was only achievable for 72 hours which is obviously not good enough and a different form of storage therefore needed to be looked at. According to The Standards Methods for the Examination of Water and Wastewater, reference 6210B, volatile organic standards can be stored for up to 4 weeks at -10 to -20°C with minimal headspace, protection from the dark and in a TFE-sealed screw-cap bottle.
All BTX standards therefore need to be stored at the above conditions for 3 weeks only. After this period fresh standards need to be prepared and ran against the old standard calibration and if they do not fall within +/-20% of the actual it could be due to either incorrect preperation of the new standards or degredation of the old standards. To check if it is the former, prepare fresh standards and recheck. If it is the latter, the storage period and conditions will need to be modified to decrease degredation. Also, if every month there is no difference between old and new standards, the storage time can possibly be increased and the standards degredation closely monitored.
All standards including the calibrating standards, the working calibration check standard and the independant QC standard need to be stored and treated in the same way.
When standards are removed from the cold storage, it is necessary to allow them to heat up to room temperature before any aliquots are removed. As there is a lot of heat generated in the laboratory it is necessary to store the standards in the refrigerator during the working day when not being used or use immediately and replace back in the freezer.

5. BLANK SAMPLES

Blank sample tubes must be included with every batch of samples for analysis. They are known as travel blanks and give an indication of background contamination effects. For every ten sample tubes there must be a travel blank which will not be exposed for sampling but only be ran in the laboratory with the sample batch.

6. QUALITY CONTROL SAMPLES

The laboratory is currently involved in The Workplace Analysis Scheme for Proficiency (WASP) which is designed to provide external quality assurance for laboratories carrying out chemical analysis of air samples taken in the workplace. Spiked tubes are recieved every 3 months both at occupational levels and enviromental levels along with two blanks and obtained results sent back to be processed. Extra tubes are ordered from the same source as the WASP tubes and the actual amounts of each analyte on each tube are known. These are then analysed under normal conditions and this allows the calibration performed to be checked. If samples deviate greatly from the expected concentrations the cause should be investigated and reported to the laboratory manager.
Replicate ATD tubes are also put out locally for a normal 30 days exposure period. These provide an estimate of the reproducibility found during the sampling of normal sample tubes

7. INTERFERENCES

Any substance which is absorbed by Tenax and may co-elute with the analytes of interest at the operating conditions used is a potential interferent.

8. TESTING EQUIPMENT

8.1 Two analytical instruments are used for BTX analysis.

1. Automatic Thermal Desorption 400 Analyser.
2. Autosystem XL Gas Chromatograph/QMass

8.1.1 Automatic Thermal Desorption 400 Analyser (ATD 400).
The ATD 400 manual is located in the GC lab and describes the the various parts of the model and explains the function of each one.
The ATD is an automatic thermal desorption system that can handle up to 50 samples. It takes each sample tube in turn, uncaps it and seals it in the carrier stream. It performs a leak test to ensure that the tube has sealed properly and heats the sample to a preselected temperature for a preselected time to extract the volatiles. The volatiles are then concentrated in a cold trap prior to transfer through a heated line to the GC column. Heating the cold trap rapidly ensures that the sample transfer is compatible with capillary columns.
The ATD has three modes of operation of which only two are used for BTX analysis.
Mode 1 is the tube conditioning mode and enables sample tubes filled with an adsorbent to be heated under controlled conditions to remove any adsorbed volatiles before it is used for sample collection. At all times the cold trap and GC column are isolated from the sample tube.
Mode 2 is the mode used for thermal desorption and hence the BTX analysis. The tubes are loaded onto the numbered carousel which rotates to the first tube position and waits until all heated zones are at their set temperatures and a ready signal is received from the GC. The sample tube is loaded into the sampling position, and the process begins.
Two split points are provided in the ATD, one before and one after the cold trap. Only one split point is used for BTX analysis.

8.1.2 Autosystem XL Gas Chromatograph.
The manual for the Autosystem GC is located in the GC lab and describes the various parts of the GC, their functions, setting the GC up for analysis and how to use the autosampler.
The Autosystem XL Gas Chromatograph is a dual-channel, temperature-programmable stand-alone GC.It is controlled using the colour-coded keyboard where you enter the operating parameters and view the prompting text. It has two injectors; a temperature programmable split/splitless injector(PSS) and an ATD 400. Each of these have seperate columns which go to two detectors: a flame ionisation detector (FID) and a mass spectrometer detector. Both columns are 25m long by 0.32mm diameter, with BPX5-0.5 (5% Phenyl polysilphenylene - siloxane) packing.
For BTX analysis, the configuration used is injection using the ATD 400, GC/MS analysis. There is no need to control either the PSS or the MS.

8. TESTING EQUIPMENTcontinued

8.1.3 Instrument Performance Verification

Before samples can be analysed, it is recommended that the instrument is checked that it is running to within acceptable limits. To do this both the calibration check BTX standard and the independant QC check BTX standard are ran as samples and quantified in the normal way assuming the stored BTX calibration is up to date and both standards are within their 3 week expiry dates. The obtained concentrations provided have to be within the control and warning limits of the relevant control charts to be acceptable. If they are, the machine is operating to an acceptable standard and samples can be analysed.

If the calibration check standard result deviates outwith the warning limit once, no action needs to be taken. If it deviates outwith the warning limit twice or outwith the control limit once, but the QC check standard is fine, prepare a fresh calibration standard and rerun. If it is then within the range, then it is safe to assume that there was an error made in the preperation of the standard initially.This also applies vice versa. If both standards deviate then it is safe to assume that it is an instrument fault and a check is required to see that all relevant parameters have been set up properly is required. A number of factors could contribute:

1. The temperature settings could be incorrect.
2. The time settings could be incorrect.
3. The tube packing or trap packing could be incorrect.
4. The pressure on either the ATD or GC could be incorrect.
5. The standard could be incorrectly prepared or degraded.
6. The split flows could be incorrect. This can happen if another analysis has been performed where the flows needed to be altered, and there is usually difficulty in trying to obtain the exact flows necessary. It is important to check that the split flows are correct before starting analysis.

If all of these are correctly set-up, repeat the BTX calibration and repeat the standards/samples run.

9. STANDARD CALIBRATION

The aim is to determine a relative standard deviation for the calibration and produce a calibration graph within the standard range.

9.1 ATD 400 conditions.

Set up the following conditions on the ATD 400: (refer to the ATD 400 Manual)

Mode	=	2
First tube	=	1
Last tube	=	1
Oven temperature	=	250°C
Desorb time	=	10mins
Valve temp	=	200°C
Trap low	=	-30°C
Trap high	=	250°C
Trap hold	=	1 mins
Trap sorbent	=	Tenax
In split	=	Yes
Out split	=	Yes
Line temp	=	200°C
Pressure (Psi)	=	12.2

9.2 ATD 400 flow rates.

The flow rates for the outlet split, inlet split and desorb flow need to be set up as follows:

9.2.1 Desorb flow/Inlet split

9.2.1.1 Put any blank tube in the number one tube position. Press the <SCROLL KEYS> key on the ATD keyboard.

9.2.1.2 Press <INSP>. It will ask for the tube position number, press 1, then enter.

9.2.1.3 Lift the lid on the back left of the instrument to get at the flow controls. Attach a bubble flow meter to the desorb flow and using the dial adjust until the flow is 16ml/min. (On the GC, press <system>, <config> <enter> and then <stopwatch> <enter>. This can be used as a flow control in conjunction with the meter).

9.2.1.4 Press <stop>.

9.2.1.5 Attach a bubble flow meter to the inlet split and using the dial adjust until the flow is 125ml/min. Press <stop>.

9.2.2 Outlet split.

9.2.2.1 Press the <SCROLL KEYS> key on the ATD keyboard.

9.2.2.2 Press <OTSP>.

9.2.2.3 Measure the outlet split at the vent to 19ml/min.

9.2.2.4 Press <stop>

With the flows set at these conditions, there will be an overall split ratio of 168:1.

9. STANDARD CALIBRATION continued

9.3 Autosystem GC conditions.
Set up the following conditions on the GC: (refer to the Autosystem GC manual)

Temperature 1	=	55°C
Time 1	=	5 min
Rate 1	=	5°C/min
Temperature 2	=	85°C
Time 2	=	1 min
Rate 2	=	0
Run time	=	12 mins
Carrier pressure	=	8 Psi

There is no need to set any other parameters as they are not involved in the analysis. They must be stable otherwise the GC wont give a ready signal.

9.4 Integrator set-up
The file number necessary to set up the BTX stored method in the integrator can be found in the ATD/GC File1 in the GC laboratory. A list of all integrator files is kept there.

9.5 Standard spiking
9.5.1 To spike a tube with the standards, attach the tube up to a GC injector and purge with carrier gas for about 5 minutes. Make sure that the tube is securely sealed. Set the carrier gas through the tube to 75ml/min using a bubble flow meter attached to the free end of the tube.
9.5.2 Inject 1ul, using a 10ul syringe which has been checked against a calibrated syringe only, of the lowest standard through the injector septa and leave for 2 minutes +/- 5 seconds using the alarmed calibrated stopwatch (EQ 258), to allow most of the solvent to evaporate off. The BTX components will remain on the tube.
9.5.3 Remove the tube and replace the caps. Place the tube on the number 1 position on the ATD 400, and press the <start> button. The tube will be put through both primary and secondary desorption once all temperatures on the ATD and the GC are stable and both give ready signals. The GC analysis and subsequent plot analysis on the integrator will only begin once the ATD has completed desorption. Total run time will be 20 minutes.
9.5.4 Four peaks will be seen on the obtained chromatogram. The first peak is the methanol remaining on the tube which is very difficult to remove totally. Benzene elutes next at 3.0-4.0 minutes, with toluene eluting at 6.5-6.7 minutes and m-xylene at 10.2-10.4 minutes. No other peaks should be present in the standard. The areas for each peak will be given in the obtained report.
9.5.5 Once the three retention times are known, proceed to calibration.

9. STANDARD CALIBRATION continued

9.6 Calibration
9.6.1 Set-up a calibration method on the integrator using the manual provided with five replicate runs of each standard being used.
9.6.2 Pre-condition 20 Tenax tubes.
9.6.3 Repeat the spiking procedure with each of the four standards, spiking 5 tubes at each level. Run as set-up so that a total of 20 chromatographic plots will be printed. The integrator automatically calculates the response factor averages at each level and provides the correlation co-efficients of each analyte. These will be printed at the end of the 20 standard runs.
9.6.4 Run a methanol blank tube with every calibration as a check for any interferences and carry over. The maximum acceptable limits for each of the three analytes detected on the blank tube is 10ng. If any are present above this concentration, then the cause needs to be investigated and eliminated before proceeding.
9.6.5 Set-up a sample table as required and all subsequent analysis runs will be quantified for BTX.

9.7 Calibration correction factors
9.7.1 To calculate the calibration correction factor for each analyte, run each standard three times and quantify as if a sample. Take the average concentration at each level for each analyte which will give four seperate figures for the four standard levels. Average the four numbers for each analyte which will provide their correction factors for the calibration.

9.8 Continuing calibration checks
9.8.1 A new calibration should be performed at least annually or more often as required. Once the calibration has been completed a calibration check comes into effect on a more routine basis where one standard in the calibrating standard range is ran as a sample and the obtained concentration should be within calculated limits against the stored calibration. This is carried out for each day of BTX analysis and with each batch of samples. Standard mix 3 is the standard that is used for the check. This check should be monitored by the use of a control chart which will include upper and lower warning and control levels which are +/-2s and +/-3s respectively where s is the standard deviation calculated from the ten replicate runs during calibration. Each time a new calibration standard is prepared a note has to be made on the control chart and the date given .
Every time a full calibration is carried out or when a calibration check standard is ran, the independant QC check standard needs to be ran also and the obtained concentration must be within the same warning and control limits. The data can be plotted on the same control form and different symbols are used to differentiate between the two standards and freshly made up standards. The control form should be displayed in the laboratory for easy reference and used forms should be kept with the Quality Manager.

9. STANDARD CALIBRATION continued

9.8.2 Run only a maximum of ten samples before running another blank and standard.
9.8 3.If a sample has a saturated peak, rerun the same tube to make sure that there will be no carryover onto the next sample.
9.8.4 If any of the three analytes are detected at concentrations greater than the highest calibration standard, prepare 2 to 3 higher range standards from the stock standard covering a range that includes the obtained concentration. Plot the calibration graph and quantify using peak area. Store the graph in ATD/GC file 1 for future reference..
9.8.4 Run a methanol blank tube with every batch of samples. Again the maximum acceptable limits for each of the three analytes detected on the blank tube is 10ng. If any are present above this concentration, then the cause needs to be investigated and eliminated before proceeding.
9.8.5 At least once every two months or more frequently if available, run a WASP QC tube as an extra check and note any deviations from the correct concentrations.

10. SAMPLE PREPERATION

For BTX analysis, there are two possible sampling techniques used. One is by trapping volatiles from the vapour phase using diffusive monitoring, where the componenets in the air migrate to the adsorbent in the tube over a period of time without the use of a sampling pump. Each analyte in BTX has a particular uptake rate on Tenax already determined by Perkin-Elmer (see Section 13). The other technique involves the use of a sampling pump to extract volatiles from the atmosphere and into the tube.
General tube and sample preperation techniques are as follows:

10.1 Sample tube packing
10.1.1 A new and unused stainless steel tube will have a stainless steel gauze fitted at the ridged end of the tube, known as the retaining gauze. Pour the Tenax into the other end of the tube (not the ridged end) using a funnel or spoon in very carefully, until it is filled to the brim.
10.1.2 Tap the tube gently to settle the adsorbent which will leave an unfilled portion of 1cm depth at the end of the tube.
10.1.3 Use the gauze loading rig to insert a second gauze in this gap, remembering not to force it down too hard. Push the plunger of the rig down only until the ball bearing spring under the tube flexes slightly. Full instructions on how to use the loading rig can be found in the ATD 400 instruction manual, located in the GC laboratory.
10.1.4 Insert a gauze retaining spring after the second gauze.
10.1.5 Clean away any adsorbent on the outside of the tube. Replace the two white caps at either end of the tube.

10. SAMPLE PREPERATION continued

10.2 Conditioning packed sample tubes
Tubes have to be conditioned after they have been freshly made up, after storage for any length of time and before sample collection.
10.2.1 Set Mode 1 on the ATD 400.
10.2.2 If freshly packed tubes, increase the oven temperature gradually over three or more successive conditioning stages until it reaches the maximum safe temperature for Tenax which is 300°C.Leave at this maximum temperature for at least 15-20minutes.
10.2.3 If stored tubes or tubes that have alraedy been analysed, condition for 15minutes at 300°C. This must always be done before tubes can be sent out for sample collection.

10.3 Storage and lifetime of packed tubes
Keep tubes capped and store in a clean enviroment at all times.If packed tubes have not been used for a period, condition before use. Unpack tubes when the packing starts to come away, clean thouroughly and repack with asdorbent. The lifetime of a packed tube can be anything from 6 months to 2 years.

10.4 Sampling
10.4.1 Sampling will be done on site by either the site chemist or the customer themselves.
10.4.2 Tubes should be sent out in batches and in labelled bags indicating tube reference numbers and location information. A log of all tubes being sent out should be kept in the laboratory by the chemist in charge.
10.4.3 A travel blank should be included for each batch of samples.
10.4.4 If diffusive monitoring - diffusive caps should be provided for each tube and the **sampling time** must be noted.
10.4.5 If pumped sampling - the **volume of air** sampled must be noted. Refer to Method MDHS 60 for the information on pumped sampling.

11. ANALYTICAL PROCEDURE

11.1 ATD 400 Conditions
Set up the following conditions on the ATD 400: (refer to the ATD 400 manual).

Mode	=	2
First tube	=	1
Last tube	=	1
Oven temperature	=	250°C
Desorb time	=	10mins
Valve temp	=	200°C
Trap low	=	-30°C
Trap high	=	250°C
Trap hold	=	1 mins
Trap sorbent	=	Tenax
In split	=	Yes
Out split	=	Yes
Line temp	=	200°C
Pressure (Psi)	=	12.2

11.2 ATD 400 flow rates
The flow rates for the outlet split and desorb flow are as follows:
11.2.1 Desorb flow - 16ml/min.
11.2.2 Inlet split - 125ml/min.
11.2.3 Outlet split - 19ml/min.

11.3 Auto system GC Conditions
Set up the following conditions on the GC: (refer to the Autosystem GC manual).

Temperature 1	=	55°C
Time 1	=	5 min
Rate 1	=	5°C/min
Temperature 2	=	85°C
Time 2	=	1 min
Rate 2	=	0
Run time	=	12 mins
Carrier pressure	=	8 Psi

There is no need to set any other parameters as they are not involved in the analysis. They must be stable otherwise the CG will not give a ready signal.

11. ANALYTICAL PROCEDURE continued

11.4 Integrator set-up.
11.4.1 Using the manual provided call up the stored BTX calibration method and set-up as indicated. Run the calibration check standard and the independant QC check standard and if the concentrations obtained are within your acceptable level, continue with sample analysis.
If BTX is detected in the sample and the integrator has printed the obtained concentrations, check that the retention times of each component corresponds to the retention times found in the check standard. It is sometimes the case that when there are a lot of peaks clustered around the actual component retention time, the integrator may not see the correct one and hence quantify the wrong peak. This does not happen very often and only if there is a lot of noise or contamination present. If it does happen though, draw the calibration graph of the analyte in question, with peak area plotted against analyte concentration and read off the amount present. The calibration graphs should be stored under ATD/GC File 1 in the GC Laboratory.
The report obtained from the integrator will have each of the BTX components concentrations, if present, on the tube in ng or calculated by hand as described above.

11.4.2 Continue to section 12 for the calculation of results.

12. CALCULATION OF RESULTS

The results obtained during quantitation are the amounts of each analyte in ng found on the sample tube These must be corrected for the density for each analyte ie. the amount of each analyte in ng must be multiplied by that particular analyte density. They are as follows:

Benzene density = 0.874
Toluene density = 0.865
m-Xylene density = 0.868

A further calculation has to be made to convert these results back to the amounts found in the original sample.

12.1 **Pumped air sampling**

The information that is required for calculation is : amount of analyte detected on the tube (in ng) (corrected for density)
: volume of air sampled in litres:
Benzene calibration correction factor
Toluene calibration correction factor
m-Xylene calibration correction factor

12.1A

$$\text{Analyte concentration in air sampled (ug/m}^3\text{)} = \frac{1000}{\text{sample vol (L)}} \times ((w - w_{blank}) \times CCF)$$

where w = weight (ug) each analyte on sample tube
w_{blank} = weight (ug) each analyte on blank tube
CCF = analyte calibration correction factor (these will change slightly with different calibrations. Note what they are store under ATD/GC File 1 in the GC Laboratory.)

12.2 **Diffusive air sampling**

The information that is required for calculation is : particular analyte uptake rate (ng/ppm/min)
: sampling time in minutes
: amount of analyte detected on the tube (in ug).
(corrected for density)
: Analyte calibration correction factor (see above)

12.2A

$$\text{Analyte concentration in air sampled (ppm)} = \frac{1000 \times ((w - w_{blank}) \times CCF)}{\text{Uptake rate (ng/ppm/min)} \times \text{Sampling time (mins)}}$$

where w = weight (ug) each analyte on sample tube
w_{blank} = weight (ug) each analyte on blank tube
CCF = analyte calibration correction factor (see above)

12.3 The calculation of BTX concentrations in diffusive air sampling may be carried out using the Lotus 123 spread sheet, file name 'BTX calc sheet' . At least one calculation from each batch of samples should be carried out manually to check the validity of the spread sheet.

13. UPTAKE RATE VALIDATION

13.1 Introduction

13.1.1 Sampling for BTX (benzene, toluene, xylene) is carried out using Perkin Elmer Automated Thermal Desorption Tubes. The tubes are packed with an absorbant packing which effectively extracts the analytes from the ambient air. For collection of BTX samples in ambient air the tubes are used in passive diffusion mode ie no pump is used. The ambient air is allowed to pass over the sampling end of the tube on which is placed a diffusion cap which is designed to ensure diffusion of the air and extraction of the analyte is consistant and reproducible. The tube is returned to the laboratory and the extracted analytes thermally desorbed and analysed. Analysis methodology is detailed in sections 3-12.

13.1.2 BTX ambient air data is reported as ppb in the sampled air. The mass of analyte found on a tube from the analysis procedure is converted to ppb data using a published uptake rate. The definition of an uptake rate is the rate at which an analyte is absorbed onto a packing from a given concentration of analyte in air. The analyte is normally also desorbed during operation of the sampler (ie it it is a reversible mechanism). For a packing to work effectively it must be compatable with the analyte - the absorption rate should be greater than the desorption rate within the operational limits of the test (eg time exposed and concentration encountered) since, if the desorption is equal to or greater than absorption, collection efficiency will be poor. The absorbant should also allow easy desorption of the analyte into the analytical system after sampling.

13.1.3 The procedure for determining uptake rate is complex and subject to many errors. Uptake rates are published by several authorities including the manufacturer (Perkin Elmer) and the Health and Safety Executive. Clyde Analytical have used published uptake rates in calculating concentrations of the analytes. Due to the difficulties involved in setting up and validating uptake rates the procedure described below was used to ensure the published uptake rates used were suitable for the application.

13.1.4 Tenax is used by the laboratory as a packing for the sampling of BTX. The packing is well established in this application but there have been reported problems associated with breakthrough of benzene. Other packings are available and it would be a relatively easy change. However, the laboratory external quality scheme (WASP) uses exclusively Tenax packing for ambient BTX calibration standards. It is therefore not possible to change the packing at present. The uptake rates used by the laboratory for toluene and xylene are partially validated to EN482 (ref CAR/Working Group 5) and are detailed in HSE Methods for the determination of hazardous substances (MDHS 50). The benzene uptake rate is validated to CEN level 1A. Some references indicate that longer sampling periods result in decreasing uptake rates (see Section 17).

13.1.5 A validation check was required for the uptake rates used.

13. UPTAKE RATE VALIDATION continued

13.1.3 This report includes validation check data for the BTX uptake rates used by Clyde Analytical.

13.1.4 The uptake rates were validated against a continuous analyser set up at West Bridge Street, Falkirk operated by Falkirk Council and monitored by Clyde Analytical Ltd.

13.2. Methodology
13.2.1 Diffusion Tubes
13.2.1.1 Perkin Elmer diffusion tubes packed with Tenax were set up at the Hope Street Car Park continuous monitoring station by Clyde Analytical Ltd. The tubes were collected and returned to the laboratory by Falkirk Council after exposure. Laboratory numbers 29264/1-5 were assigned to the samples

13.2.1.2 Analysis was carried out according to accredited procedure ATD1.1. and concentrations calculated using the uptake rate detailed in Table 1.

Table 13.1

Uptake Rates

Analyte	Uptake Rate ng/ppm/min
Benzene	1.3
Toluene	1.7
Xylene	2.4

13. UPTAKE RATE VALIDATION continued

13.2.2 BTX Continuous Monitor
13.2.2.1 Benzene, toluene and xylene were measured at the monitoring station using a Horiba APPA-360 BTX analyser.

13.2.2.2 A fixed volume of ambient air was absorbed onto a concentration tube which was subsequently heated and the BTX passed to a GC column via a stripper column. The separated components were passed to a photoionisation detector and the BTX quantified.

13.2.2.3 The procedure is a reference method.

13.2.2.4 Calibration was by permeation generator checked against an NPL standard.

13.2.2.5 Clyde Analytical are linked by modem to the station and benzene data for the exposure period was downloaded.

13.3. Results
13.3.1 ATD tube data is detailed in Table 13.1. Station data is detailed in Table 13.2 and 13.3.

Table 13.2

ATD Tube

Sample	Benzene		Toluene		Xylene		Notes
	ng	ppb*	ng	ppb	ng	ppb	
Replicate 1	73	1.7	222	3.3	202	2.2	
Replicate 2	56	1.3	166	2.5	133	1.5	
Replicate 3	160	3.7	0	0	1298	14.1	End caps off tube. Data discard
Replicate 4	66	1.5	232	3.5	222	2.4	
Average	65	1.5	207	3.1	186	2	
Standard Dev	-	0.2	-	0.5	-	0.5	

* based on uptake rate of 1.3 ng/ppm/min
Data corrected for travel blank

13. UPTAKE RATE VALIDATION continued

13.3. Results continued.

Table 13.3

Station Data

24 Hour Mean Values

Date	Benzene ppb	Toluene ppb	Xylene ppb
27/11/98	5.124	8.456	7.904
28/11/98	1.223	2.735	1.106
29/11/98	1.399	2.854	1.210
30/11/98	2.538	5.204	2.849
1/12/98	1.514	3.592	1.732
2/12/98	2.462	5.770	3.183
3/12/98	1.633	3.610	1.926
4/12/98	0.950	1.911	0.377
5/12/98	1.256	2.247	0.547
6/12/98	2.234	4.066	1.947
7/12/98	6.836	11.51	12.45
8/12/98	1.259	3.060	1.313
9/12/98	1.386	2.890	1.270
10/12/98	1.520	2.945	1.656
11/12/98	2.712	5.395	4.146
12/12/98	1.630	3.536	1.331
13/12/98	0.867	1.637	0.722
14/12/98	0.479	0.881	0.727
15/12/98	0.615	1.053	0.289
16/12/98	0.199	0.448	1.561
17/12/98	0.292	0.125	1.268
Average	1.82	3.5	2.36

13.4. **Comments**

13.4.1 Comparative data is given in Table13.4.

Table 13.4

Comparative Data

Analyte	Diffusion Tube		Automatic Station	
	Result ppb	**SD**	**Result** ppb	**SD***
Benzene	1.5	0.2	1.82	0.15 @ 4.7
Toluene	3.1	0.5	3.5	0.25 @ 7.85
Xylene	2.0	0.5	2.36	o- 0.10 @ 2.45
				m- 0.05 @ 1.60
				p- 0.10 @ 3.05

* National Physical Laboratory data

13.4.2 The data shows that in a real outside field sampling situation over several weeks, active and passive sampling produces comparable data and good correlation at low concentrations. The data produced by the laboratory appears to be fit for the purpose, especially considering the current environmental limits for benzene is 5 ppb, toluene 489 ppb and xylene 1000 ppb.

13.5. Recommendations

13.5.1 The use of the partially validated uptake rate for benzene for environmental applications given in the literature is not appropriate since the data would produce a poorer correlation with the active sampler eg use of 0.86 ng/ppm/min would give a benzene concentration of 2.3 ppb.

13.5.2 The current uptake rates for benzene, toluene and xylene should continue to be used.

13.5.3 The uptake rate validation procedure shall be repeated annually.

14. RECOVERY AND LOSSES FROM EXPOSED TUBES

14.1 **Introduction**

14.1.1 Uptake rate validation procedure and sampling mechanism of diffusive samplers is described in Section 13. Direct comparison of atmospheric concentrations of BTX using a different technique showed good correllation using the Perkin Elmer uptake rates.

14.1.2 This section describes work to estimate losses from exposed tubes in the situation of an initial exposure of a diffusion tubes to a very high concentration of analyte followed by exposure to a low concentration for the remaining sampling period.

14.1.3 The mechanism of absorption onto a packing in a diffusion tube is essentially reversible (it would be impossible to carry out the analysis if the analyte was permanently attached to the packing).

14.1.4 It would therefore be expected that the spiking of an ATD tube at a high loading followed by exposure to a low or zero concentration would result in analyte desorption and losses. The process of losing analyte from a diffusion tube is known as back diffusion

14.1.5 The reference document for assessing the performance of diffusive samplers ("Protocol for assessing the performance of a diffusive sampler" - MDHS27 (rev Feb 1994) HSE) does not address the problem of back diffusion. However the HSE/CAR Working Group 5 have published a paper (1) which indicates that the relative overall uncertainty using 12 set experiments and exposing to zero air ranges from 24-46% depending on initial exposure. The reductions and errors were attributed to back diffusion. The experiments were carried out on a 7 day standard exposure followed by a 7 day zero air exposure so results are not directly comparable. However the general trend and data was found to be similar. The paper states that the error was acceptable according to CEN requirements for workplace air monitoring.

14.2 **Procedure**

14.2.1 Six ATD tubes were positioned outside at Mentor Gardens. Adjacent traffic was low density. Tubes were treated as detailed in Table 14.1 Spiking was carried out according to the standard preparation procedure described in Section 9. The tubes were treated as standard laboratory samples and included a blank.

Table 14.1

Tube Spiking

Reference	Benzene Spike ng	Toluene Spike ng	Xylene Spike ng
31455/1	Blank	Blank	Blank
31455/2	250	500	500
31455/3	250	500	500
31455/4	0	0	0
31455/5	0	0	0
31455/6	250 after exposure	500 after exposure	500 after exposure
31455/7	250 after exposure	500 after exposure	500 after exposure

14.2.2 The tubes were exposed over the period 21st September - 20th October 1999

14.3 **Results**

14.3.1 The analysis results are detailed in Table 14.2.

Table 14.2

Results

Reference	Benzene ng	Toluene ng	Xylene ng
31455/1	-	-	-
31455/2	160	451	463
31455/3	131	386	459
31455/4	35	85	70
31455/5	25	70	59
31455/6	249	553	549
31455/7	262	593	576

14.4 **Comments**

14.4.1 It is reasonable to expect that back diffusion occurs during diffusive sampling. The literature (1) indicates the extent of back diffusion during long term environmental sampling. Based on initial sampling period and calculating a loading on the tubes after 7 days exposure to each concentration, Table 14.3 shows effective initial loading prior to being exposed to 7 days clean air and analyte decrease due to back diffusion.

Table 14.3

Calculated Loadings And Back Diffusion From Literature

Calculated Loading After Exposure ng	Calculated Loading On Tube After Exposure To Zero Air ng	% Decrease
53	40	24
66	54	17
264	193	27
1320	818	38
1518	820	46
2903	1626	44

14.4.2 At the calculated loading of 264 ng freom the literature (close to the 250-500 ng spiked loadings given in Table 14.1) the decrease would be expected to be in the order of 27% over 7 days according to the published data.

14.4.3 The decrease for 250 ng loading of benzene over a 28 day period was 42%, the decrease for 500 ng loading of toluene was 16% and the decrease in xylene concentration was 8%.

14.4.4 The back diffusion of toluene and xylene was lower than for benzene (note only data for benzene was included in the literature).

14.4.5 Data indicates that the back diffusion rate decreases with time. However, note that the residual background BTX concentrations would also affect back diffusion rate to some extent.

14.5 **Conclusions**

14.5.1 It has been demonstrated that back diffusion occurs from diffusion tubes over extended exposure periods. Benzene is most affected by the process. Toluene and xylene are less affected. The measured back diffusion rate is comparable to that quoted in the literature.

14.5.2 The significance of the data is that an initial exposure to a very high benzene concentration (equivalent to 192,000 ppb assuming a 1 minute exposure) would suffer a bias of 42% decrease over a 28 day exposure period in a typical low traffic density site with correspondingly low BTX concentrations

14.5.3 Benzene concentrations in high traffic sites generally do not exceed 5 ppb. Toluene and xylene concentrations are sometimes slightly higher.

14.5.4 Continuous monitoring data (West Bridge St, Falkirk) indicates average BTX concentrations vary relatively slowly with time and the daily averages are consistant.

14.5.5 It is therefore unlikely that back diffusion would be a significant problem during ambient BTX sampling. However, in situations where very high concentrations lead to initial loadings of BTX in excess of 250-500 ng of each analyte on the diffusion tube followed by a long exposure to zero or low concentrations, back diffusion may result in a significant bias in the data.

14.5.6 It is possible that back diffusion of benzene may be reduced by changing the tube packing. However the WASP quality scheme uses only Tenax for quality system samples. Until an alternative packing is used in the WASP scheme an assessment of errors due to back diffusion will be required for applications other than ambient surveys or where analyte concentrations will not vary greatly due to operational practices.

(1) The use of diffusive samplers for measuring benzene at ppb levels in the environment. Saunders KJ. BP International Ltd, Sunbury on Thames.

15. PRECISION AND BIAS

15.1 For precision and bias figures, see table 15.1:

Analyte	Spiking Conc (ng)	Mean Conc (ng)	No of replicates	Standard deviation/ Precision %	Mean Recovery %
Benzene	250	259	10	+/- 3.9	104
Toluene	500	512	10	+/- 4.1	102
m-Xylene	500	517	10	+/- 4.4	103

Table 15.1

16. DETECTION LIMITS

The detection limit for each analyte is as follows assuming a sampling time of 30 days:

Benzene = 20ng on tube = 0.4ppb in atmosphere
Toluene = 40ng on tube = 0.5ppb in atmosphere
m-xylene = 40ng on tube = 0.5ppb in atmosphere

The precision and bias data at this level can be found in table 16.1:

Analyte	Spiking Conc (ng)	Mean Conc (ng)	No of replicates	Standard deviation/ Precision %	Mean Recovery %
Benzene	20	20	10	+/- 4.8	100
Toluene	40	53	10	+/- 6.8	132
m-Xylene	40	45	10	+/- 6.9	112

Table 16.1

17. UNCERTAINTY OF MEASUREMENT

17.1 The procedure used to calculate test uncertainties is detailed in the General Laboratory Procedures Manual.

17.2 Uncertainties associated with the measurement of BTX in ambient air are detailed in table 17.1.

Analyte	Estimated Test Uncertainty
Benzene	+/- 11.6 ng
Toluene	+/- 20.2 ng
Xylene	+/- 27.6ng

Table 17.1

18. COSHH ASSESSMENTS/HEALTH AND SAFETY

18.1 COSHH Assessment
See relevant COSHH assessment form.

18.2 Health and Safety
Workplace monitoring of the laboratory levels of solvent is carried out internally and on a regular basis. This involves the set-up of Tenax ATD tubes throughout the laboratory over a normal working day and the levels monitored closely to check that they are within the allowable TLV's. All results are kept with the Quality Manager.

19. REFERENCES

19.1 Perkin-Elmer LC1-100 Integrator Manual.

19.2 Perkin-Elmer Autosystem Gas Chromatograph User's Manual.

19.3 Perkin-Elmer ATD 400 User's Manual.

19.4 Perkin-Elmer Thermal Desorption Application - No 2.
No 33.
No 40.

19.5 Perkin-Elmer Thermal Desorption Data Sheet - No 3.
No 10.

19.6 Standard Methods for the Examination of Wastewater and Water - method reference 6210 B

19.7 Mixed hydrocarbons (C_3-C_{10}) in air - method reference MDHS 60.

19.8 EN482 (ref CAR/Working Group 5), HSE Methods for the determination of hazardous substances - method reference MDHS 50.

19.9 Peters R and Hafkenscheid, Diffusive Monitor, 7, 8-9 (1995).

19.10 Brown, Crump, Gardiner, Yu, Long Term Diffusive Sampling Of VOC's in indoor air.

19.11 Environmental Technology 14, 771-777, 1993.

19.12 Diffusive Uptake Rates On Perkin-Elmer Sorbent Tubes CAR/WG 5, The Diffusive Monitor Issue 8 Sept 1996.

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NITROGEN DIOXIDE ANALYSIS OF AIR

METHOD REFERENCE AIR 1

1. Introduction and Scope

1.1 This method describes the preparation and analysis of sample tubes designed to measure the airborne concentration of nitrogen dioxide in the atmosphere.
1.2 The range of measurement for colorimetric analysis is 0.2 - 4 ppm
1.3 The range of measurement for airborne concentration depends on the exposure period of the sample tube.

2. Principle

Sample tubes are treated with a triethanolamine absorbent prior to exposure.
The nitrogen dioxide collected on the tube during exposure is absorbed as nitrite by a variant of the Saltzman reaction. The nitrite reacts with sulphanilamide and N-1-naphthyethylenediamine dihydrochloride, under acidic conditions, to form a reddish purple azo dye. The intensity of the purple colour is determined spectrophotometrically at 540nm and the concentration of nitrite is determined from a calibration graph of absorbance against concentration. The nitrogen dioxide concentration can then be calculated from the nitrite concentration found in the tube, the exposure time and a constant.

3. Testing Equipment

3.1 Nitrogen dioxide tube are supplied by Gradko International Ltd:
- 100 white caps (cat no DIFCAP-001)
- 100 red/blue caps (cat no DIFCAP-002)
- 100 acrylic 71mm moulded tubes
- 100 stainless steel mesh discs

3.2 1ml graduated pipette.
3.3 2ml graduated pipette.
3.4 5ml graduated pipette.
3.5 1ml bulb pipette.
3.6 2ml bulb pipette.
3.7 4ml bulb pipette.
3.8 SP6-500 UV spectrophotometer capable of reading at 540nm.
3.9 2 x Matched cells with a unique reference number. Procedure for matching the cells can be found in the NO2 file 1 located in the GC lab.
3.10 Calibrated stopwatch - EQ 208.

4. Environmental Control

4.1 Testing should be carried out in a clean environment.

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5. Interferences

5.1 The working NEDA solution may absorb NO_2 from the atmosphere, so it must therefore be covered when not in use. There are no other documented interferences for this method.
5.2 Samples which have been interfered with should be discarded.

6. Standards

6.1 Calibration Standards

Grade A glassware must be used for all standard preparation
6.1.1 100ppm stock nitrite standard
Dissolve 0.15 +/-0.01g of sodium nitrite (dried at 100 +/-5°C) in 1 litre of deionised water and mix well. This solution may be kept for 1 year. Label with expiry date, assign a reference number and initial. Record the details of source, batch etc on the standards log found in the NO2 file 1 located in the GC lab.
6.1.2 Working Calibration Standards
All standards should be prepared using grade A bulb pipettes. Three working standards of 1ppm, 2ppm and 4ppm nitrite are required. All working standards should be prepared prior to use and each one assigned a relevant reference.
6.1.2.1 1ppm working standard - Pipette 1ml stock standard into a 100ml grade A volumetric flask and make up with deionised water.
6.1.2.2 2ppm working standard - Pipette 2mls stock standard into a 100ml grade A volumetric flask and make up with deionised water. This standard is also used as a continuing calibration check standard.
6.1.2.3 4ppm working standard - Pipette 4ml stock standard into a grade A 100ml volumetric flask and make up with deionised water.

6.2 Independant Calibration Check Standard

All standards should be prepared using grade A bulb pipettes.
6.2.1 Prepare a 100ppm stock nitrite standard as described in 6.1 using sodium nitrite from a different source. Label with expiry date, assign a reference number and initial. Record the details of source, batch etc on the standards log found in the NO2 file 1 located in the GC lab.
6.2.2 Prepare a 2ppm QC check standard by pipetting 2mls, from a bulb pipette, of the 100ppm stock standard into a grade A 100ml volumetric flask and make up with deionised water. Assign a relevent reference. Check standard should be made up prior to use.

7. Reagents

7.1 All reagents must be kept refrigerated and made up fresh every year or more often as required. Label each one with expiry date and initials of chemist involved in preparation.
7.2 Absorbent
Measure 40ml of triethanolamine into a 200ml measuring cylinder and add 0.05ml BRIJ 35 using a 1ml graduated pipette. Make up to 200ml with deionised water. Shake to mix.
7.2 Sulphanilamide/Phosphoric acid reagent
Measure 50ml phosphoric acid in to a measuring cylinder and add to approx 800ml deionised water. Mix well. Add 20 +/- 1g sulphanilamide and mix to dissolve. Make up to 1 litre in a grade A volumetric flask.

7. Reagents continued

7.3 NEDA stock solution

To approx 80ml deionised water add 0.14 +/- 0.01g N-1-naphthyethylenediamine dihydrochloride (NEDA) and mix well to dissolve. Make up to 100ml in a grade A volumetric flask.

7.4 NEDA working reagent

Using a measuring cylinder, add 150ml sulphanilamide/phosphoric acid reagent and 15ml stock NEDA to 150ml deionised water. Mix well.

8. Calibration

8.1 Annual Calibration

Standards should be made up using grade A bulb pipettes.Each standard is analysed in triplicate.

8.1.1 Switch on the spectrophotometer operating at 540nm and leave to warm up for at least 30 minutes.

8.1.2 Prepare 10 tubes as described in section 9

8.1.3 Into three of the tubes, pipette 1ml of the 1ppm nitrite standard.

8.1.4 Into another three, pipette 1ml of the 2ppm nitrite standard.

8.1.5 Into another three tubes, pipette 1ml of the 4ppm nitrite standard.

8.1.6 Into the tenth tube, pipette 1ml of deionised water. This is the blank.

8.1.7 Into all ten tubes pipette 2ml working NEDA solution and mix.

8.1.8 Allow all the tubes to stand for 30-40 minutes (+/- 5mins) to allow full colour development. This time should be measured using a calibrated stopwatch.The presence of nitrite is indicated by a pink colour.

8.1.9 To a clean cuvette, add the blank and insert into the spectrophotometer. Zero the machine if necessary.

8.1.10 Read the absorbance of each of the standards three times and take the average. Set the blank to zero between each reading if necessary.

8.1.11 Fill out the standards control sheet available for each standard and calculate the standard deviation. Calculate the %RSD also which must be less than 20% to be acceptable.

8.1.12 A calibration factor for each standard must also be calculated as follows:

$$\text{Calibration Factor (CF)} = \frac{\text{Mean absorbance of standard}}{\text{Amount of standard}}$$

8.1.13 Take the mean calibration factor of the three standards and calculate the standard deviation. Find out the linear range of the calibration as follows:

$$\text{RSD \%} = \frac{\text{Standard deviation}}{\text{mean CF}} \times 100$$

Put all the information into the calibration certificate sheet provided, and if the RSD obtained is <20%, then the calibration is acceptable. Assign the calibration with an appropriate reference.

8.1.14 Draw a calibration graph, plotting the nitrite concentrations (in ppm) against absorbances. Assign the calibration graph with a relevant reference.

8.1.15 All data generated should be stored in the file with reference NO_2 -file 1 in the GC laboratory.

8.1.16 The date of calibration should be recorded on the control chart .

8. Calibration ctd

8.2 Preparation of Control Charts

A control chart should be prepared as follows:

8.2.1 Prepare five replicate tubes and spike with the 2ppm standard.

8.2.2 Analyse as normal and calculate the nitrite concentrations in ppm for each tube from the calibration graph..

8.2.3 Calculate the mean nitrite concentration in ppm and the standard deviation of the five replicates and plot a control chart where the upper and lower warning limits are (x2) the SD, and the upper and lower control limits are (x3) the SD.

8.3 Continuing Calibration

8.3.1 With each batch of samples, analyse both the 2ppm calibration standard and also the additional independant 2ppm check standard. This is a check for both instrument performance and standard and reagent degradation. The obtained concentrations provided have to be within the control and warning limits of the relevant control charts to be acceptable. If they are, the machine is operating to an acceptable standard and samples can be analysed.

If the calibration check standard result deviates outwith the warning limit once, no action needs to be taken. If it deviates outwith the warning limit twice or outwith the control limit once, but the QC check standard is fine, prepare a fresh calibration standard and rerun. If it is then within the range, then it is safe to assume that there was an error made in the preperation of the standard initially.This also applies vice versa. If both standards deviate then it is safe to assume that it is an instrument fault and a check is required to see that all relevant parameters have been set up properly is required.

8.3.2 Mark the concentrations obtained on the control chart along with the date and analyst initials.

9. Analytical Procedure

9.1 Preparation of tubes

9.1.1 New Tubes

9.1.1.1 New tubes purchased from Gradko are already prepared with the triethanolamine absorbent. Retain a blank tube for each batch sent to customers and use as the blank when analysing the samples once they have been returned to the laboratory.

9.1.1.2 The caps and tubes may be reused, after careful cleaning. The discs must be cleaned in detergent, rinsed with tap water, then deionised water and finally with acetone. They are then dried in a 105 +/-5°C oven.

9.1.2 Used Tubes

9.1.2.1 Into a red cap place 2 stainless steel discs. Use a graduated 1ml pipette to transfer 0.05ml absorbent onto the red cap.

9.1.2.2 Push the ridged end of a moulded tube into this red cap gently to ensure that the absorbent does not splash up the sides of the tube. Insert a white cap onto the other end of the tube.

9.1.2.3 Label the tubes with a marker pen.

9.1.2.4 Once prepared, send immediately to the customer in sealed bags or store in a refrigerator between 2-8°C. Provide sample worksheets to the customer also, to be completed before the tubes are sent back to the laboratory.

9.1.2.5 Use within 6 weeks of preparation

9.1.2.6 Prepare a blank tube with each batch of tubes made up. Store in the fridge and analyse with the batch of samples when they are returned to the laboratory. This must be used as the blank during analysis.

9.2 Sample analysis

9.2.1 Uncap the blank tube made up with the batch of samples and, using a bulb pipette, transfer 1ml of deionised water into it.

9.2.2 Using a 5ml graduated pipette, transfer 2ml of working NEDA solution into the blank tube and mix well. Note this start time in a workbook..

9.2.3 Using a 5ml graduated pipette, transfer 3ml of working NEDA solution into each sample tube, and mix well. Note this end time in a workbook.

9.2.4 Allow all the tubes to stand for 30-40 minutes (+/- 5mins) to allow for colour development. This time period should begin when the NEDA solution has been added to the first tube and should be measured using a calibrated stopwatch.

9.2.5 To a clean cuvette, add the blank and insert into the spectrophotometer. Zero the machine if necessary.

9.2.6 Read the absorbance of each sample and record in work book.. Note the start and end time of absorbance measurement in a workbook to ensure that you are within the relevant time tolerance. Set the blank to zero between each reading if necessary.

9.2.7 If the sample is found to be over the calibration range, prepare a 5ppm standard or above and run along with the sample. Extend the calibration graph as appropriate and read off sample absorbance

10. Calculation of Results

10.1 Read each sample absorbance off the calibration graph and therefore obtain the nitrite concentration in ppm.

10.2 Use the following calculation to obtain the NO_2 concentration in ppb:

$$\textbf{Nitrogen dioxide (ppb)} = \frac{\textbf{7258 x conc in ppm (from graph)}}{\textbf{Sample exposure time (hours)}}$$

10.3 The nitrogen dioxide concentration is usually given in ug/m3. Conversion as follows:

Nitrogen dioxide (ug/m3) = conc in ppb x 1.88

11. Quality control

11.1 Internal

11.1.1 For each batch of samples, both a 2ppm working calibration standard and an extra check standard should be analysed and the result plotted on the control chart as in 7.B

11.1.2. For each batch of samples every tenth sample should be read in triplicate and an average absorbance taken.

11.1.3 An ongoing validation check should be performed by comparing the monthly concentrations of the passive NO_2 tube set up at the Municipal Buildings at Falkirk District Council against their continous NO_2 sampling monitor figures. These comparisons can then be plotted on a graph and looked at more closely.

11.2 External - monthly

11.2.1 Quality control samples from External Proficiency Testing (PT) schemes arrive in the laboratory on a monthly basis to be analysed in conjunction with the normal monthly survey samples. Two samples are analysed:

QC sample 1 - Doped tube spiked with a known amount of nitrite.
Result not known by the laboratory before analysis.
Tube is posted each month from WASP.

QC sample 2 - Nitrite standard solution in the range 1900-2000mg/l is supplied by AEA Technology every six months.
Exact concentration of the standard known initially and used as an additional calibration check..
Standard is refrigerated in the laboratory for 6 months and then discarded
Solution requires x1000 dilution before analysis.

Both of the above are analysed along with the normal samples and the results posted to WASP and AEAas soon as possible. Records must be kept of all results obtained and stored in the relevant Proficiency Testing Scheme file. On receipt of a PT report, a QC report sheet must be completed and signed by the Quality Manager.

11. Quality control continued

11.3 External - annually

11.3.1 The laboratory also participates in an annual Field Intercomparison Excercise which is carried out by AEA TEchnology. NO_2 tubes supplied by Clyde Analytical are exposed in a controlled environment for a four week period. The tubes are then returned to the laboratory for subsequent analysis. The results are then posted to AEA Technology who then generate a full intercomparable report. The results and obtained data associated with this excercise are stored in file ref NO_2 File 1 in the GC lab.

11. Precision and Bias

11.1 Doped tubes

For precision and bias figures for doped tubes, see table 11.1:

Analyte	Spiking Conc (ppm)	Mean Conc (ppm)	No of replicates	Standard deviation/ Precision %	% Bias	Mean Recovery %
Nitrite	2.00	1.96	5	+/- 2.0	- 2.0	98

Table 11.1

11.2 Exposed tubes

For precision and bias figures for exposed tubes, see table 11.2:

Analyte	Actual measurement (ppb)	Mean measurement (ppb)	No of replicates	Standard deviation/ Precision %	% Bias	Mean Recovery %
Nitrite	19.0	18.2	6	+/- 1.6	- 4.3	96

Table 11.2

12. Detection Limit

The detection limit for nitrite on a tube is 0.2ppm, therefore assuming a sampling period of 30 days the detection limit for nitrite in atmosphere is 4ug/m^3. The precision and bias figures for these levels can be found in table 12.1:

Analyte	Spiking Conc (ppm)	Mean Conc (ppm)	No of replicates	Standard deviation/ Precision %	% Bias	Mean Recovery %
Nitrite	0.20	0.20	5	+/- 9.5	0.0	100

Table 12.1

13. Uncertainties

See Document - METHOD UNCERTAINTIES for details on sources of uncertainty in the measurement of NO_2.

14. COSHH

See relevant COSHH assessment.

15. References

15.1 The measurement of Nitrogen Dioxide in the Outdoor Environment using Passive Diffusion Tube Samplers - reference AERE-R12133. February 1986.

15.2 Summary Results from the UK NO2 Network Field Intercomparison Exercise 1999 - AEA Technology Environment 1-12 Issued (2). 19 April 2000.

VALIDATION CHECK REPORT

Sample Reference
Grangemouth

5 Replicate nitrogen dioxide diffusion tubes exposed at the continous monitor at Falkirk District Council (FDC). To be used as a comparative check for both nitrite recovery and reproducibility.

Date Received	18/09/00
Report Date	18/10/00
Sampled By	Prepared by Clyde Analytical and put out for exposure by FDC
Delivered By	Post
Exposure Period	04/08/00 - 13/09/00

Sample Description

33750/1-5. Nitrogen Dioxide diffusion tubes - Warren Springs approved design.

Analysis

Diffusion tubes - Tricthanolamine/Brij 35 absorbant, NEDA colorimetric reaction. Spectrophotometric determination. According to Warren Springs provided methodology.

Continous monitor - Nitric oxide (NO) reacts with ozone to form nitrogen dioxide (NO_2). The reaction produces energy as light and is specific to nitric oxide with few or no interferences from other gaseous components. The intensity of the light produced is proportional to the concentration of NO. The Horiba APNA-360 separates the samples gas into two proportions. In one portion, NO_2 is reduced to NO by the NO_x converter and the NO in the sample measured. In the other, the NO sample gas is analysed directly. Individual NO and NO2 concentrations can be presented.

Results

NO2 Passive Samplers			Grangemouth Continous Monitor
Mean Nitrite Conc (ppb)	SD	RSD %	Mean Nitrite Conc (ppb)
9.5	0.44	2.4	10.7

Comments

The mean nitrite concentration for the passive diffusion tubes was calculated using 5 replicate tubes.
The mean nitrite for the continous monitor was calculated using the 24hour averages for the exposure period used.
Correlation between the two tests is acceptable.

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Technical Director

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