UK Ambient Hydrocarbon Non-Automatic Air Quality Network:

Report on Pilot Study of Manually Pumped and Diffusive Sampling Techniques for Benzene Measurement

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1. INTRODUCTION AND BACKGROUND

This report has been prepared for the Department for the Environment, Food and Rural Affairs (formerly DETR) by NPL and HSL under contract EPG 1/3/161.

To fulfil the UK's EC requirements for ambient benzene measurements, the number of benzene monitoring sites will need to increase from the 13 operating in 2000 to around 36. The automated Chrompack and Perkin-Elmer gas chromatographs at the 13 sites have delivered good quality hourly data for 25 hydrocarbon species (including benzene and 1,3-butadiene), but at substantial operating and data ratification costs.

The EC requirement is for long-term average measurements (reported as annual averages) of benzene alone. The reference method is specified as pumped sampling of ambient air followed by analysis by gas chromatography. This can be done by automated instruments such as the ones above, or by simpler sampling systems whose samples are analysed later in a laboratory. Details of standard reference methods are to be set down as CEN standards by Working Group 13 of CEN Technical Committee 264.

Methods used by member states to monitor benzene must produce results equivalent to those of the reference method, and comply with the data quality objectives, in terms of measurement uncertainty, data capture and time coverage.

In 2000 NPL proposed that the UK use a pumped sampling method taking 7-day samples of ambient air. DETR chose to assess this proposal during a Pilot Study running approximately from September 2000 to August 2001, with NPL systems running alongside the 4 continuing automated sites.

The Pilot Study also contained parallel measurements of benzene, toluene and xylenes using four-weekly diffusive sampling, carried out by HSL under contract to NPL. The technique differs from pumped sampling essentially only in the mechanism of sampling ambient air. In diffusive sampling, the sampled volume is calculated via an empirically determined diffusive uptake rate, as opposed to the volume passing through a calibrated pump during pumped sampling, and is about a factor of 20 lower in this instance.

NPL also has extensive experience of diffusively sampled benzene measurement, and to provide extra information to the Pilot Study included its own parallel diffusive measurements, made fortnightly, at no extra cost.

The first part of this Report covers NPL's work, and includes comparisons between measurements from the different measurement techniques including the automated instruments operated by AEA Technology. The preliminary report on the first six months of HSL's work is given as a self-contained annex, along with the complete years data set.

2. PRELIMINARY LABORATORY WORK ON THE PUMPED METHOD

Early decisions on the pumped method concerned two areas – the design and parameters of the pump unit, and the choice of sorbent material within the sampling tube. The sampling tubes were standard Perkin Elmer design, for compatibility with automated analysis instruments.

2.1 Pump Unit

No suitable complete pump unit was available. NPL therefore designed and built 8 units using standard components.

To build an accurate, stable and reliable pumping system, it was decided that the unit would be based on pumping through a mass flow controller. The main benefit of using a mass flow controller is that changes in sample volume caused by changing ambient temperature and pressure are automatically corrected. Therefore, the flow measurements can be directly reported at 293 K and 101.3 kPa, as required by the benzene directive. The other advantage of a mass flow controller is that it avoids variations in sample flow caused by changes in pump behaviour – the pump is only required to produce an adequate pressure drop across the mass flow controller. NPL uses mass flow controllers in many aspects of its measurement work and finds them to be very stable and reliable.

A flow rate of 10 ml/min was chosen. Although mass flow controllers can operate accurately at lower flow rates, this rate is commonly used for pumped sampling elsewhere.

An important early decision was to switch the flow regularly between two separate sampling tubes, every few minutes. This has two main benefits:

- For a given sampling volume per tube, the sampling time in the field is doubled. We therefore aimed to leave the unit pumping unattended for two weeks instead of one, with each tube sampling around 100 litres of ambient air, with consequent savings in Local Site Operator visits.

- The twin tubes, although sampling sequentially, are expected to sample near-identical concentrations over the fortnight. The technique therefore provides an excellent QA check through duplicate measurements, without the expense of duplicate pump units.

The pump units were also equipped with several simple diagnostic features, such as a timer, which would indicate if the power had failed during the measurement period, and a "health check" circuit, which confirmed the continuing correct operation of the mass, flow controller.

2.2 Choice of sorbent

Pumped sampling techniques are limited by the rate at which the benzene migrates along the sorbent material in the tube as it is pumped. To prevent the benzene being carried through the pumping end of the sampling tube, the pumped volume needs to be kept well below the breakthrough volume for the particular sorbent and pollutant. Commonly used sorbents for benzene have breakthrough volumes of a few tens of litres, but the range of sorbents available has increased in recent years. The other critical factor is the ability to remove all the sampled benzene from the sorbent using readily achievable temperatures and flow rates on automated thermal desorption instruments, prior to injection into the gas chromatograph.

Early laboratory tests were therefore done on many different sorbents to determine breakthrough volumes, both in dry and wet conditions, desorption efficiency and general analytical factors, such as the effect of absorbed water.

Carbopack X was chosen as the preferred sorbent. From the laboratory tests the breakthrough volume was determined to be in excess of 500 litres with both dry and wet test gas. This compares with the sampled volume of approximately 100 litres per sampler. Desorption efficiency was determined to be virtually 100%. Further tests determined the stability of the benzene – sorbent matrix and thus the shelf life of tubes from the end of sampling to subsequent analysis. The results showed a maximum loss of 1% of the sampled mass of benzene over a one month period. This is the maximum delay between sampling and analysis that might conceivably occur; in practice this delay will be much shorter.

Other laboratory tests were performed to determine the effects of interferents including water. The results showed a maximum effect of 1%.

The results from these laboratory tests, as well as other information such as the manufacturer's specifications for the mass flow controllers, were used to construct the uncertainty budget for the pumped method, given in Section 6.

3. PRELIMINARY FIELD WORK ON THE PUMPED METHOD

The first pump units, and the analytical method, were initially trialled at NPL, alongside the Chrompack instrument operating on the site. A few early trials were also done at Marylebone Road to observe higher concentrations.

The full results are given in Table 1. Analysis of the pumped tubes yields a quantity of benzene in nanograms, calibrated against standard liquid solutions of benzene added to similar (but unexposed) tubes analysed in the same sequence. The ambient concentration in ng/m^3 is therefore directly calculated from the average of the two duplicate tube nanogram values and the volume of air sampled, given by the mass flow controller rate and the elapsed time.

The spread column is simply the difference between the two duplicate values expressed as a percent of the average value.

Table 1 - Preliminary pumped benzene results

Site	Period	Volume	Benzene	Benzene	Spread	Average	Auto	% pump
		litres @ 20C	tube A (ng)	tube B (ng)	%	pumped ppb	ppb (mean)	from auto
Teddington	20/10/00 - 23/10/00	107.5	155	153	1.3	0.44	0.49	-10.0
	23/10/00 - 30/10/00	107.7	45	44.6	0.9	0.13	0.14	-8.6
	30/10/00 - 6/11/00	107	104	106	1.9	0.30	0.34	-11.2
	2nd pump unit:	107.1	108	106	1.9	0.31	0.34	-9.6
	6/11/00 - 20/11/00	107.1	201	193	4.1	0.57	0.62	-8.7
	2nd pump unit:	107.1	203	219	7.6	0.61	0.62	-2.2
	28/11/00 - 5/12/00	107.9	85.4	84.5	1.1	0.24	0.21	15.4
	2nd pump unit:	107.9	79.3	83.5	5.2	0.23	0.21	10.5
Marylebone	8/11/00 - 22/11/00	109	1202	1219	1.4	3.42	3.16	8.1
Road								
	29/11/00 - 6/12/00	108.3	1003	1011	0.8	2.86	2.44	17.3

These results showed very good consistency between the duplicate tubes, between different pump boxes, and between the pumped method and the automatic method over a wide range of concentrations.

4. RESULTS FROM MEASUREMENTS AT NETWORK SITES

The benzene concentration data collected by the NPL pumped tube method and the NPL diffusive method is summarised in Tables 2 and 3. HSL data is presented in the same way for comparison.

As in Table 1, the “spread” values in Table 2 refer to the difference between the pairs of duplicate measurements – two independent tubes in the case of diffusive samplers – expressed in absolute concentration or as a percent of the average value. Aside from the crucial issue of accuracy, any useful method must of course give closely similar results for duplicate measurements of the same air sample.

Table 2 Spread of benzene data collected by the NPL pumped tube method, the NPL diffusive method and the HSL diffusive method.

	NPL Pumped		NPL Diffusive		HSL Diffusive	
	PPB	**%**	**PPB**	**%**	**PPB**	**%**
Spread – all sites						
Average spread between tubes	0.02	3.1	0.06	9.1	0.07	8.5
Standard deviation of spread	0.03	3.9	0.09	13.6	0.08	9.8
Max Spread	0.23	30.3	0.32	43.8	0.40	48.8
Min Spread	0.00	0.0	0.00	0.0	0.00	0.0

Table 3 presents all the data in terms of averaged concentrations, comparing methods as directly as possible, though data capture from the automatic method is sometimes low.

Table 3 Comparison of average benzene values determined by the NPL Pumped Tube Method, the NPL Diffusive Method and the HSL Diffusive Method

	NPL Pumped		NPL Diffusive		HSL Diffusive	
	PPB	**%**	**PPB**	**%**	**PPB**	**%**
Cardiff						
Method average	0.54		0.46		0.53	
Automatic average	0.55		0.55		0.56	
Difference from automatic method	-0.01	-1.8	-0.09	-16.4	-0.03	-4.8
Max Difference (absolute)	0.13	17.7	0.53	71.9	0.13	17.1
Min Difference (absolute)	0.00	0.0	0.01	3.9	0.02	1.6
Number of samples	26		26		13	
Edinburgh						
Method average	0.35		0.37		0.42	
Automatic average	0.41		0.45		0.46	
Difference from automatic method	-0.06	-14.6	-0.08	-17.8	-0.04	-8.7
Max Difference (absolute)	0.14	41.9	0.21	55.0	0.14	40.9
Min Difference (absolute)	0.00	0.0	0.00	0.0	0.00	0.0
Number of samples	21		26		13	
Harwell						
Method average	0.20		0.24		0.27	
Automatic average	0.19		0.21		0.19	
Difference from automatic method	0.01	5.3	0.03	14.3	0.08	38.9
Max Difference (absolute)	0.08	41.9	0.14	38.9	0.23	127.8
Min Difference (absolute)	0.00	0.0	0.01	2.04	0.02	15.4
Number of samples	27		23		13	
Marylebone Road						
Method average	2.03		1.62		1.73	
Automatic average	1.65		1.56		1.62	
Difference from automatic method	0.38	23.0	0.06	3.8	0.11	6.8
Max Difference (absolute)	0.69	32.9	0.85	100.1	0.50	23.6
Min Difference (absolute)	0.03	2.0	0.02	1.6	0.03	2.0
Number of samples	23		25		14	
All sites						
Method average	0.75		0.67		0.75	
Automatic average	0.67		0.70		0.74	
Difference from automatic method	0.08	11.9	0.03	4.3	0.01	1.4
Number of samples	97		100		53	
All sites except Marylebone Road						
Method average	0.36		0.36		0.41	
Automatic average	0.38		0.41		0.40	
Difference from automatic method	-0.02	-4.4	-0.05	-12.9	0.01	0.8

Figures 1 to 4 present all the data as time series comparisons between the pumped method and the automatic data.

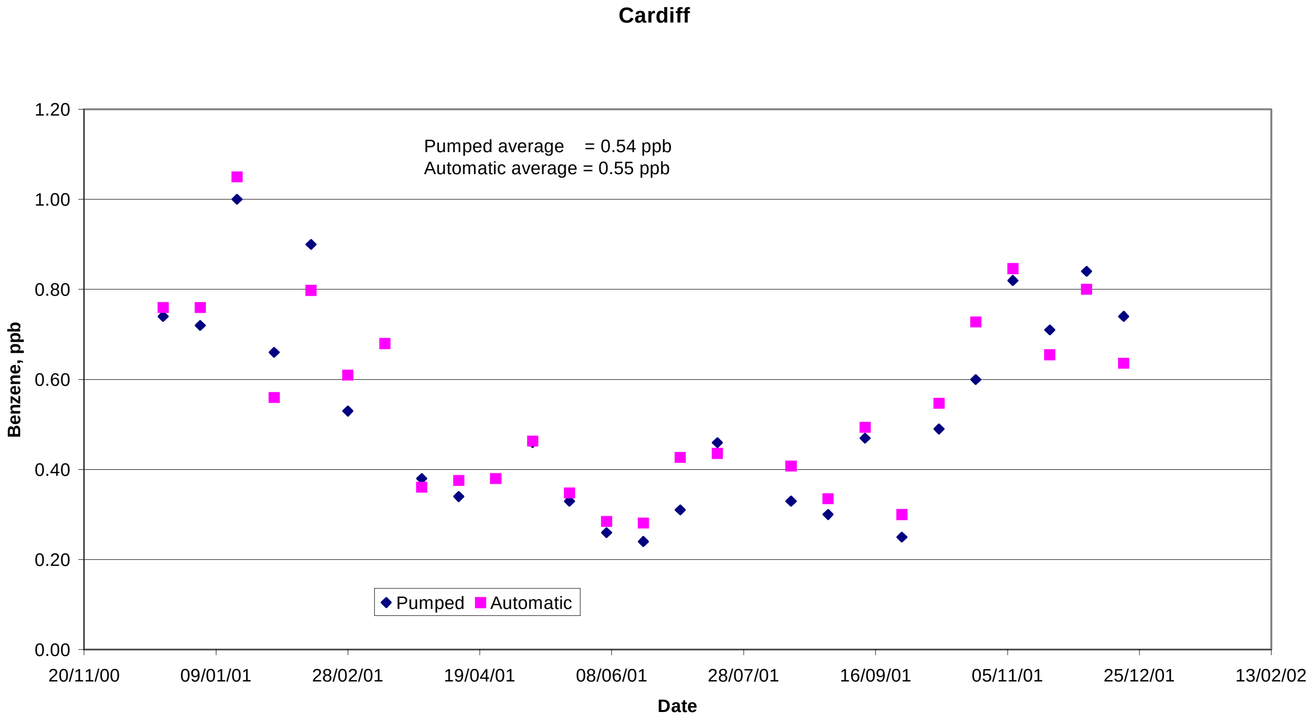

Figure 1

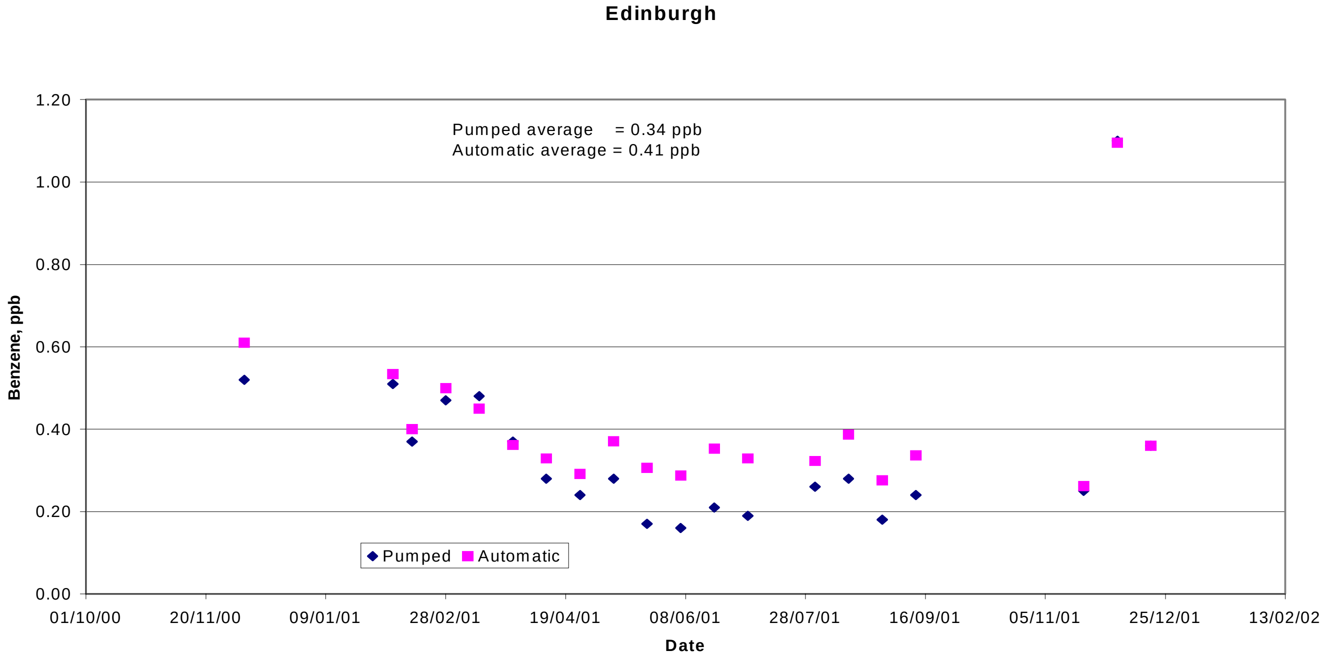

Figure 2

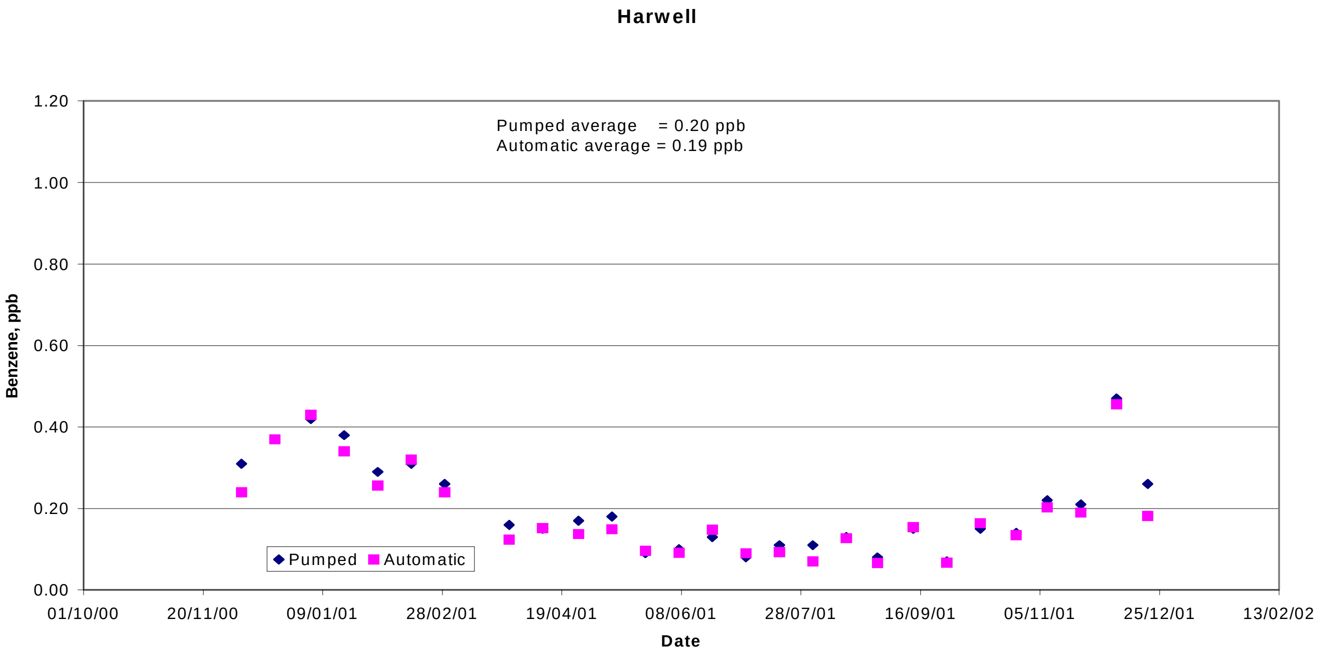

Figure 3

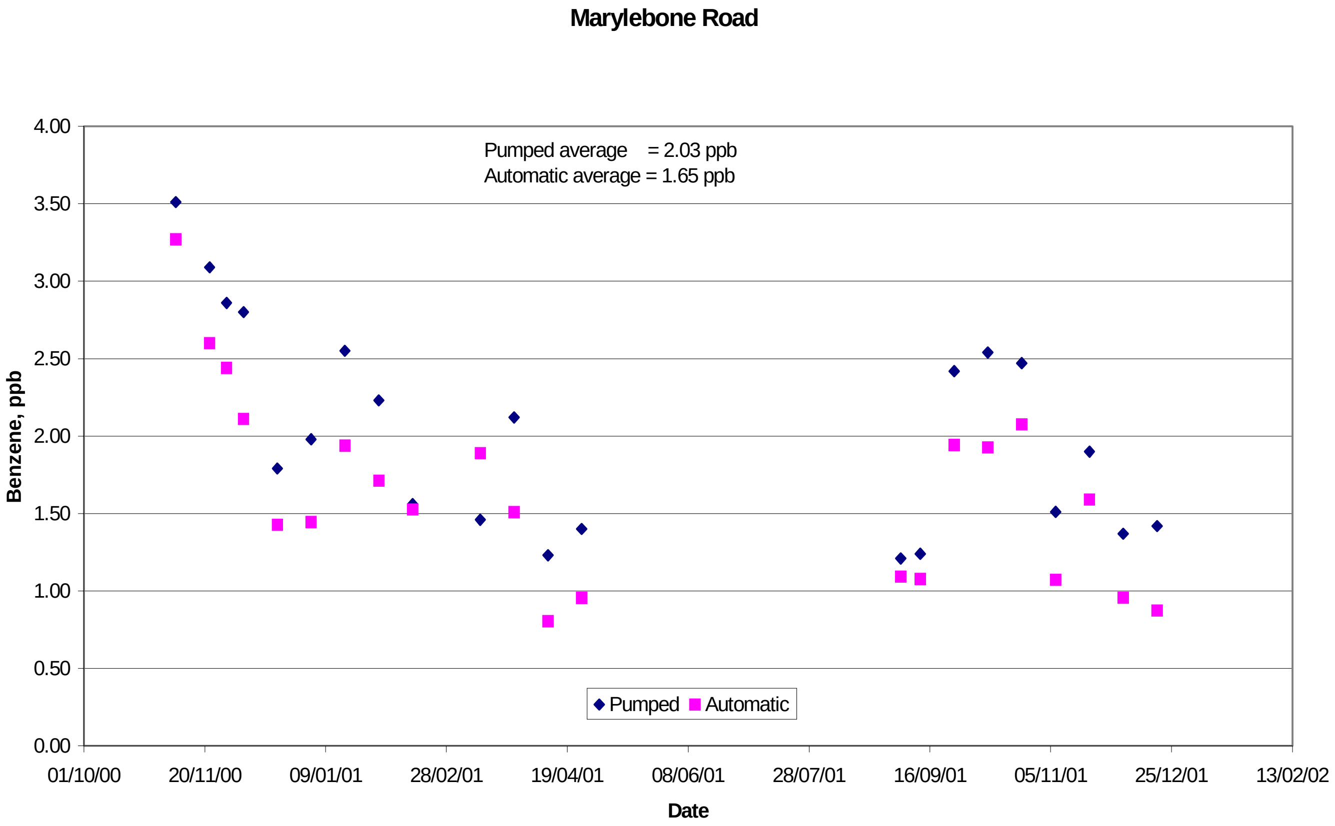

Figure 4

The complete set of data collected by the NPL pumped and diffusive methods is contained in Annex 1, and complete set of data collected by the HSL diffusive method is contained in Annex 3.

The results for the pumped and automatic methods generally agree very well within the uncertainties of both methods at Cardiff and Harwell.

At Edinburgh there is some evidence of a systematic difference between the two methods, with the pumped method reading lower by an average of 0.06 ppb over the whole period, rising to around 0.1 ppb for a period between May and August. Both sets of diffusive measurements tend to agree with the pumped measurements. The cause of this may be simply the slight difference in sampling points for the different methods.

There is a more significant systematic difference in the data from Marylebone Road, where the pumped method consistently averages 0.4 ppb more than the automatic method. Given the rather simple calibration method for the pumped method, and the fact that it is hard to conceive how benzene might be over-collected by the pumped tubes, rather than lost or under-collected, we suspect that the difference is due to one of the special factors at the Marylebone Road site - high concentrations, rapidly changing concentrations, a Perkin Elmer rather than a Chrompack automatic instrument - rather than the pumped method. This view is supported by tests undertaken on the site by NPL in February 2002, reported to DEFRA in a letter dated 18 April 2002, which indicate that the difference is consistent with a non-linearity in the Perkin Elmer instrument which would make it underread when concentrations fall below about 1 ppb.

5. CONTROLLED ATMOSPHERE TESTS

NPL operates a controlled atmosphere test facility (CATFAC), capable of exposing pumped and diffusive sampling systems to accurately known concentrations of pollutants at ambient concentrations in controlled conditions of temperature, humidity and air flow for long periods. The concentration within the CATFAC is determined by comparison with NPL hydrocarbon gas standards.

As part of the Pilot Study, the facility was used to help evaluate the pumped benzene system. Three pump units, exposing a total of 6 sample tubes, were operated while the CATFAC ran at a constant benzene concentration close to the EC limit value, 1.55 ± 0.04 ppb, at a temperature of 10°C, relative humidity of 50%, a flow of 0.5 m/s, over a period of 2 weeks.

The results from the three pump units were:

Unit	Concentration	Spread
A	1.64 ppb	0.6%
B	1.60 ppb	0.6%
C	1.53 ppb	1.3%

Where “spread” has the same definition as used earlier.

The mean benzene concentration derived from the pumped systems was 1.59 ppb, a value that differs from the CATFAC value by less than 3%.

Further validation of the pumped benzene system was performed during a European intercomparison of diffusion methods for benzene. The CATFAC facility was run at different benzene concentrations and relative humidities, and the pumped benzene sampler set to sample for a two-week period at each concentration. The results are summarised below:

Relative Humidity, %RH at 21°C	50.0 ± 5	50 ± 5	50 ± 5	50 ± 5	90 ± 5
Applied concentration, PPB	0.69	1.45	7.66	0.17	1.77
Measured concentration, PPB	0.70	1.44	7.58	0.19	1.87
Difference, PPB	0.01	-0.01	-0.08	0.02	0.10
Difference, %	1.3	-0.6	-1.0	9.6	5.4

These tests show that the difference between the measured concentration by the pumped benzene sampler and the applied concentration is less than 10% for all concentrations levels that would be expected to occur in the ambient atmosphere, and less than about 5% for concentrations over 2 ppb. These differences are all within the calculated measurement uncertainty of 11.5%, derived in section 6.

With the artificially constant conditions, results might be expected to be more self-consistent than those from site studies. However, the very good agreements obtained are further direct validation of the:

- Reproducibility of pump unit performance
- Equal exposure of the “duplicate” tubes
- Repeatability of the desorption and analysis processes
- Calibration of the pumped method – which is entirely independent of the CATFAC calibration.

6. PERFORMANCE IN COMPARISON WITH BENZENE DIRECTIVE DATA QUALITY OBJECTIVES

6.1 Uncertainty

The measurement uncertainty for the pumped tube method was calculated following the method laid out in the CEN working document [1], which conveniently uses pumped sampling of benzene as an example in Annex D. The numbers used in that document are for demonstration purposes, and the numbers here relate specifically to NPL’s pumped system, which for example has better flow control than in the CEN example. Table 4 breaks down the uncertainty components into those contributing to the uncertainty in sample volume and those contributing to the uncertainty of the mass of benzene collected.

Table 4 Uncertainty Of Pumped Method

Source	**Assessment**	**Value**	**Probability Distribution**	**Divisor**	**% Standard Uncertainty**
Volume of sampled air					
Sample time		2%	Rectangular	√3	1.155
Flow rate accuracy	1% full scale	2%	Rectangular	√3	1.155
Flow rate repeatability	0.2% full scale	0.4%	Normal	1	0.4
Drift in flow	2% in six months	2%	Rectangular	√3	1.155
Pressure correction	0.02% full scale / psi, assume a 3% range	0.02%	Normal	1	0.02
Temperature correction	0.13% full scale / deg C, assume a 10C range	2.6%	Normal	1	2.6
Analytical					
Sampling efficiency	Insignificant	0			0.000
Stability of benzene / sample matrix	Tested by GC lab	1%	Normal	1	1.000
Non-recovery of Benzene on desorption	Insignificant	0	Normal		0.000
Analytical repeatability	13118 measurements	3.522%	Normal	1	3.522
Linearity	Experimental tests	3%	Rectangular	√3	2.887
Interference	Experimental tests	1%	Rectangular	√3	0.577
Blank	<2ng ≡ 0.01PPB, assume limit value (1.5 PPB)	0.67%	Rectangular	√3	0.386

Providing the individual components contribute independently and linearly to the final measurement result, the combined standard uncertainty (equivalent to one standard deviation) is calculated from the root sum of the squares of the components.

These conditions apply in this case, giving a combined standard uncertainty of 5.8% at the limit value of 1.6 ppb.

For an approximately 95% level of confidence (as required by the benzene directive), a factor of 2 is applied to the standard uncertainty, giving a total combined expanded uncertainty of 11.5%.

This uncertainty is for a single tube measurement using the pumped tube method. It will not necessarily reduce when more than one measurement is averaged. Therefore, a conservative estimate of the total combined expanded uncertainty of the annual mean is also 11.5%, expressed with a level of confidence of 95%.

The total combined uncertainty for the pumped tube method, is lower than half of that required by the EU Benzene Directive for mandatory measurements.

The uncertainty of 11.5% for the pumped method is considerably better than the uncertainty for diffusive methods, which we estimate to be approximately 22% on a similar basis.

This determination of measurement uncertainty from first principles should be compared with actual field results to assess whether all uncertainty components have been considered and scaled correctly. Given that ratified automatic data is associated with expanded uncertainties of around 10%, the actual average differences from the Pilot Study results are quite consistent with the calculated uncertainties.

6.2 Data Capture And Time Coverage

Data capture for the pumped benzene method was 86%. The main reasons for data loss were: the absence of sampling periods, from 20/12/00 to 31/01/01 and 12/09/01 to 20/11/01, at the Edinburgh site and the loss of data between 09/05/01 and 03/09/01 at Marylebone Road.

The first data gap at Edinburgh occurred because the LSO disassembled the Swagelok elbow fitting (which should not normally be done), and did not replace the O-ring at reassembly. This was difficult to diagnose and consequently was not corrected immediately. An NPL site visit and LSO re-training rectified this fault, and the problem should not reoccur at any site. The second data gap was due to the partial failure of the sample pump. This fault was not immediately detected, as the reported concentrations did not differ significantly from the diffusive or automatic measurements. An extra diagnostic check, by the LSO at their fortnightly visit, has been introduced to aid in the early detection of this fault, if it should occur again.

The data gap at Marylebone Road occurred due to an internal plumbing fault introduced buy a routine service of the pump box. This fault was detected at the next service visit and the same diagnostics check introduced to monitor the sample pump will also remove the possibility of this fault occurring again.

The remaining data loss was due to the failed analysis of one of the tubes making up a sample pair. All of NPL’s reported concentration data are the average of the two tubes in a sample pair. If one of the tubes clearly fails to produce a valid result, then no concentration result is reported.

The time coverage for the pumped benzene method is 100%.

Data capture for the NPL diffusive benzene method was 88%. The data loss was due to the failed analysis of one of the tubes making up a sample pair. All of NPL's reported concentration data are the average of the two tubes in a sample pair. If one of the tubes clearly fails to produce a valid result, then no concentration result is reported.

The time coverage for the NPL diffusive benzene method was 100%.

7. RECOMMENDATIONS FOR NETWORK OPERATION AND QA/QC

7.1 LSO Matters

The mechanics of sending and receiving samplers by post has been set up with very few problems. LSOs were all trained by NPL staff and have a copy of the LSO manual, included in this report as Annex 4. HSL have produced a similar LSO manual for their diffusive sampling requirements.

7.2 Pump Unit maintenance and calibration

We propose to visit all sites every six months to calibrate the mass flow controller, check or change sampling lines, and carry out other functional checks on the items at sites, as described in NPL's original proposal.

Pump unit reliability has so far been very good. We propose initially that where any problems develop, the normal action will be to replace the entire pump unit and repair any faults at NPL.

7.3 Analytical QA/QC

NPL has UKAS accreditation for hydrocarbon analysis of sorbent tubes, and follows rigorous procedures for analysis, calibration and data handling. This will continue to form the basis for QA/QC of the analysis.

8. SUMMARY AND CONCLUSIONS

- As expected, the "spread" of duplicate sets of pumped data (3.9%) is significantly lower than that for both sets of diffusive data (about 12%), presumably due to the better control of sampled volume, and the larger quantities of benzene being analysed. This is a valuable measure of the repeatability of whole methods in real conditions.

- Agreement between the pumped system and the automatic system is better than 10% at Cardiff (1.8%) and Harwell (5.3%). At Edinburgh, the pumped method averages about 15% less than the automatic average, equivalent to 0.06 ppb, while the two sets of diffusive results tend to agree with the pumped results. This may be due to sampling or calibration issues. At Marylebone Road, the pumped method averages about 23% more than the automatic average, or about 0.4 ppb. This difference is probably due to the non-linearity of the site GC at low concentrations, as detailed in the letter to the department dated 18th April 2002.

- The Pilot Study has been valuable in highlighting some unexpected operational problems concerning the tube connections and pumping system. Procedures have been modified so that future data capture should meet the EC requirement of 90%.

- When operating the pumped method under artificially constant conditions the difference between the measured concentrations reported by the pumped benzene sampler and the applied concentrations are less than 5% for all concentrations above 0.2 ppb.

- The provisional measurement uncertainty for the pumped tube method, expressed with a level of confidence of 95%, is 11.5%. This is considerably better than the comparable uncertainty for diffusive methods, which we estimate to be approximately 22%, expressed with the same level of confidence.

- Drawing together the findings from the laboratory and field studies, the pumped tube method appears to be a simple, practical and reliable method for meeting the requirements of the EC Daughter Directive on ambient benzene measurement.

9. REFERENCES

[1] Comité Européen de Normalisation. Air Quality – Approach to uncertainty estimation for ambient air reference methods. CR 14377 Jan 2002

ANNEX 1 DATA COLLECTED BY THE NPL PUMPED AND DIFFUSIVE METHODS

NPL Pumped Benzene Data

Site	Date	Pumped ppbA	Pumped ppbB	Pumped spread (%)	Pumped PPB
Cardiff					
	20/12/00	0.75	0.73	2.97	0.74
	03/01/01	0.72	0.72	0.23	0.72
	17/01/01	0.98	1.01	3.69	1.00
	31/01/01	0.65	0.68	4.76	0.66
	14/02/01	0.94	0.87	7.36	0.90
	28/02/01	0.53	0.53	0.23	0.53
	14/03/01	0.67	0.69	2.83	0.68
	28/03/01	0.37	0.39	5.00	0.38
	11/04/01	0.33	0.36	7.97	0.34
	25/04/01	0.39	0.38	1.72	0.38
	09/05/01	0.46	0.47	0.23	0.46
	23/05/01	0.30	0.36	16.93	0.33
	06/06/01	0.28	0.24	14.97	0.26
	20/06/01	0.24	0.23	5.57	0.24
	04/07/01	0.30	0.31	5.15	0.31
	18/07/01	0.52	0.41	23.84	0.46
	15/08/01	0.33	0.33	1.22	0.33
	29/08/01	0.30	0.30	0.30	0.30
	12/09/01	0.47	0.48	2.30	0.47
	26/09/01	0.24	0.26	4.26	0.25
	10/10/01	0.50	0.49	2.31	0.49
	24/10/01	0.59	0.61	2.21	0.60
	07/11/01	0.82	0.81	0.45	0.82
	21/11/01	0.73	0.69	5.15	0.71
	05/12/01	0.86	0.82	4.45	0.84
	19/12/01	0.79	0.70	11.29	0.74
	02/01/02	0.81	0.83	2.15	0.82
Edinburgh					
	06/12/00	0.51	0.52	2.53	0.52
	06/02/01	0.50	0.52	4.03	0.51
	14/02/01	0.36	0.39	7.15	0.37

Site	Date	Pumped ppbA	Pumped ppbB	Pumped spread (%)	Pumped PPB
	28/02/01	0.47	0.47	0.00	0.47
	14/03/01	0.47	0.50	7.01	0.48
	28/03/01	0.38	0.36	4.13	0.37
	11/04/01	0.28	0.29	3.56	0.28
	25/04/01	0.24	0.24	2.50	0.24
	09/05/01	0.27	0.30	11.27	0.28
	23/05/01	0.17	0.17	1.15	0.17
	06/06/01	0.18	0.15	19.13	0.16
	20/06/01	0.21	0.20	2.87	0.21
	04/07/01	0.20	0.17	15.94	0.19
	01/08/01	0.25	0.26	1.39	0.26
	15/08/01	0.28	0.29	1.72	0.28
	29/08/01	0.18	0.18	0.12	0.18
	12/09/01	0.23	0.25	8.53	0.24
	08/11/01	0.26	0.27	7.09	0.26
	21/11/01	0.25	0.24	6.12	0.25
	05/12/01	1.09	1.10	0.68	1.10
	19/12/01	0.36	0.36	1.02	0.36
Harwell					
	06/12/00	0.30	0.32	5.03	0.31
	20/12/00	0.37	0.37	0.44	0.37
	04/01/01	0.41	0.42	2.03	0.42
	18/01/01	0.39	0.38	2.29	0.38
	01/02/01	0.30	0.29	1.57	0.29
	15/02/01	0.32	0.31	1.68	0.31
	01/03/01	0.25	0.26	2.14	0.26
	28/03/01	0.15	0.17	10.91	0.16
	11/04/01	0.15	0.15	3.40	0.15
	26/04/01	0.16	0.18	12.32	0.17
	10/05/01	0.17	0.18	6.40	0.18
	24/05/01	0.08	0.09	8.53	0.09
	07/06/01	0.09	0.11	21.79	0.10
	21/06/01	0.13	0.14	8.81	0.13
	05/07/01	0.07	0.08	14.30	0.08
	19/07/01	0.11	0.11	2.50	0.11
	02/08/01	0.10	0.11	1.35	0.11
	16/08/01	0.14	0.13	2.42	0.13
	29/08/01	0.08	0.08	2.53	0.08
	13/09/01	0.15	0.16	9.03	0.15
	27/09/01	0.07	0.07	2.28	0.07
	11/10/01	0.15	0.16	3.83	0.15
	26/10/01	0.14	0.14	1.50	0.14
	08/11/01	0.20	0.23	11.36	0.22

Site	Date	Pumped ppbA	Pumped ppbB	Pumped spread (%)	Pumped PPB
	22/11/01	0.22	0.20	8.53	0.21
	07/12/01	0.46	0.48	4.32	0.47
	20/12/01	0.26	0.26	0.17	0.26
Marylebone Road					
	08/11/00	3.48	3.53	1.40	3.51
	22/11/00	3.11	3.06	1.68	3.09
	29/11/00	2.85	2.87	0.82	2.86
	06/12/00	2.80	2.80	0.10	2.80
	20/12/00	1.80	1.78	1.33	1.79
	03/01/01	1.98	1.99	0.48	1.98
	17/01/01	2.57	2.52	1.85	2.55
	31/01/01	2.21	2.25	1.80	2.23
	14/02/01	1.58	1.53	3.10	1.56
	28/02/01	1.78	1.80	0.68	1.79
	14/03/01	1.35	1.58	15.60	1.46
	28/03/01	2.18	2.07	5.40	2.12
	11/04/01	1.26	1.20	4.83	1.23
	25/04/01	1.42	1.37	3.63	1.40
	04/09/01	1.17	1.26	6.82	1.21
	12/09/01	1.21	1.27	5.09	1.24
	26/09/01	2.41	2.42	0.35	2.42
	10/10/01	2.55	2.53	0.72	2.54
	24/10/01	2.47	2.47	0.13	2.47
	07/11/01	1.51	1.51	0.00	1.51
	21/11/01	1.87	1.93	3.14	1.90
	05/12/01	1.38	1.36	1.35	1.37
	19/12/01	1.41	1.42	1.21	1.42

NPL Diffusive Benzene Data

Site	Diffusive Start Date	Diffusive ppb A	Diffusive ppb B	Diffusive spread (%)	Diffusive PPB
Cardiff					
	07/11/00	0.68	0.74	9.03	0.71
	21/11/00	0.36	0.36	0.00	0.36
	06/12/00	0.53	0.48	10.49	0.50
	20/12/00	0.72	0.50	35.78	0.61
	03/01/01	0.93	0.88	5.27	0.91
	17/01/01	0.79	0.76	3.64	0.78
	31/01/01	0.53	0.52	2.77	0.53
	14/02/01	0.67	0.75	11.74	0.71
	28/03/01	0.30	0.35	15.54	0.33
	11/04/01	0.38	0.40	4.56	0.39
	25/04/01	0.41	0.45	8.74	0.43
	09/05/01	0.42	0.56	28.14	0.49
	23/05/01	0.25	0.27	7.72	0.26
	06/06/01	0.31	0.35	11.44	0.33
	20/06/01	0.27	0.25	9.62	0.26
	04/07/01	0.32	0.30	6.48	0.31
	18/07/01	0.21	0.21	2.25	0.21
	15/08/01	0.32	0.36	11.68	0.34
	19/08/01	0.16	0.16	4.40	0.16
	12/09/01	0.47	0.45	3.15	0.46
	26/09/01	0.26	0.23	15.36	0.25
	10/10/01	0.41	0.46	11.69	0.44
	24/10/01	0.29	0.12	80.96	0.20
	07/11/01	0.76	0.69	10.12	0.72
	05/12/01	0.68	0.72	4.82	0.70
	19/12/01	0.62	0.52	16.48	0.57
Edinburgh					
	23/11/00	0.36	0.32	11.89	0.34
	06/12/00	0.46	0.38	19.35	0.42
	20/12/00	0.34	0.36	4.26	0.35
	03/01/01	0.91	0.84	7.46	0.87
	17/01/01	0.69	0.73	5.72	0.71
	31/01/01	0.45	0.45	0.53	0.45
	14/02/01	0.36	0.33	9.84	0.35
	28/02/01	0.43	0.44	1.38	0.43
	14/03/01	0.31	0.39	20.91	0.35
	28/03/01	0.35	0.38	8.10	0.36
	11/04/01	0.34	0.37	8.44	0.35

Site	**Diffusive Start Date**	**Diffusive ppb A**	**Diffusive ppb B**	**Diffusive spread (%)**	**Diffusive PPB**
	25/04/01	0.25	0.28	10.54	0.27
	09/05/01	0.24	0.28	15.00	0.26
	23/05/01	0.19	0.13	35.85	0.16
	06/06/01	0.19	0.21	11.49	0.20
	04/07/01	0.22	0.24	7.52	0.23
	18/07/01	0.18	0.16	8.97	0.17
	15/08/01	0.32	0.34	7.81	0.33
	29/08/01	0.22	0.20	11.82	0.21
	13/09/01	0.27	0.29	6.23	0.28
	26/09/01	0.19	0.23	17.80	0.21
	10/10/01	0.40	0.39	3.25	0.40
	24/10/01	0.23	0.21	9.60	0.22
	07/11/01	0.31	0.24	25.32	0.28
	05/12/01	1.02	0.93	9.29	0.97
	19/12/01	0.34	0.35	2.41	0.35
Harwell					
	14/11/00	0.21	0.25	16.33	0.23
	24/11/00	0.24	0.18	27.52	0.21
	06/12/00	0.35	0.25	32.83	0.30
	20/12/00	0.25	0.20	21.75	0.23
	04/01/01	0.46	0.54	15.44	0.50
	18/01/01	0.41	0.26	46.08	0.33
	01/02/01	0.25	0.29	16.38	0.27
	15/02/01	0.28	0.26	4.70	0.27
	01/03/01	0.25	0.24	5.02	0.25
	15/03/01	0.40	0.35	12.06	0.38
	28/03/01	0.20	0.22	8.91	0.21
	11/04/01	0.18	0.22	20.89	0.20
	26/04/01	0.15	0.18	16.58	0.17
	10/05/01	0.14	0.20	35.61	0.17
	07/06/01	0.13	0.17	28.83	0.15
	05/07/01	0.11	0.11	0.00	0.11
	16/08/01	0.12	0.21	55.27	0.16
	13/09/01	0.17	0.15	11.38	0.16
	27/09/01	0.11	0.07	46.68	0.09
	11/10/01	0.17	0.12	36.80	0.15
	08/11/01	0.25	0.22	10.28	0.23
	07/12/01	0.35	0.41	15.28	0.38
	20/12/01	0.21	0.35	50.63	0.28

Site	Diffusive Start Date	Diffusive ppb A	Diffusive ppb B	Diffusive spread (%)	Diffusive PPB
Marylebone Road					
	08/11/00	3.49	3.59	2.75	3.54
	22/11/00	2.33	2.41	3.14	2.37
	06/12/00	2.40	2.23	7.35	2.32
	20/12/00	1.40	1.31	6.88	1.35
	03/01/01	2.14	1.96	8.52	2.05
	17/01/01	2.49	2.60	4.13	2.54
	31/01/01	1.90	1.79	5.65	1.84
	14/02/01	1.54	1.63	5.53	1.59
	28/02/01	1.84	1.56	16.77	1.70
	14/03/01	1.20	1.21	1.43	1.20
	28/03/01	1.34	1.34	0.58	1.34
	11/04/01	1.21	1.23	1.09	1.22
	25/04/01	1.19	1.19	0.09	1.19
	09/05/01	1.63	1.31	21.92	1.47
	23/05/01	1.22	1.31	7.12	1.27
	06/06/01	1.32	1.35	1.58	1.34
	04/07/01	1.52	1.65	8.27	1.59
	18/07/01	1.05	1.05	0.06	1.05
	15/08/01	1.56	1.36	13.76	1.46
	29/08/01	1.04	1.10	4.85	1.07
	12/09/01	0.98	1.08	10.25	1.03
	26/09/01	1.94	1.83	5.77	1.89
	10/10/01	1.78	1.06	50.16	1.42
	24/10/01	1.39	1.32	4.89	1.36
	07/11/01	1.19	1.21	2.09	1.20

ANNEX 2 PRELIMINARY REPORT BY HSL ON BENZENE DIFFUSION TUBE MEASUREMENTS

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UK Non-Automatic Hydrocarbon Network
BTEX Diffusive Sampling

Report for DEFRA meeting
Thursday 19 July 2001

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1. Summary

This report summarises the data obtained to date from the pilot study according to year 1 of the HSL subcontract schedule 1 to Contract S009801. The sites concerned are Edinburgh, Cardiff, Harwell and Marylebone.

Under the terms of the (sub)contract, DETR (now DEFRA) requires additional validation/ confirmation of the:

- Measurement uncertainty
- Data capture
- Time coverage
- Required QA/QC.

It may also be possible to assess the equivalency of the three procedures to be used in the pilot study – diffusive benzene as conducted by HSL, pumped benzene as conducted by NPL and BTEX analyser as conducted principally by NETCEN. However, HSL does not have direct access to the NPL data and the analyser data is often incomplete.

On the basis of theoretical calculations (following CEN guidance), the expanded uncertainty of measurements of benzene performed by the diffusive sampler method has been shown to be concentration-dependent. In all cases, however, it is within the data quality objectives set in the Benzene Daughter Directive. These theoretical calculations are supported by empirical estimates of uncertainty based on the paired sampling data, and unpublished data from HSE/CAR/WG5.

The data capture and time coverage have both been 100% so far in the pilot study and are well within the requirements of the Directive and DETR guidance.

During the period of the pilot study, HSL has consistently achieved Category 1 status in the WASP external quality assurance scheme for this type of analysis.

Recommendations for any future rejection of paired data are given on the basis of the uncertainty calculations.

2. General

Written instructions have been provided for Local Site Operators [1]. This guidance is complementary to that provided by the Department [2]: Chapter 3: Monitoring for benzene.

The analysis procedure, calibration and system checks and diffusive uptake rates were as described in the first monthly interim report [3]. However, since the draft CEN standard prEN 13528-2 no longer contains experimental diffusive uptake rates, reference is instead made to the more comprehensive list in reference [4], which is also quoted in [2].

Carbograph TD-1 (manufactured by Carbochimica Romana) has been used in preference to Chromosorb 106 because it has an uptake rate for benzene that is closer to the theoretical maximum value. Its physical properties are indistinguishable from Carbopack B.

Large labels on the transport boxes containing diffusive tubes are now printed in a simple form style, so the LSOs can record exposure start/stop times on the box. The site identity is also printed on the label to facilitate handling within HSL. This will become more important in the main study. On future labels we will add ***4-weeks*** in a prominent position to minimise the accidental changeover at 2-weeks which has happened at two sites.

3. Measurement uncertainty

It was anticipated that experimental data would be available on the measurement uncertainty for diffusive sampling of benzene from the minimum validation programme to be conducted by CEN/TC264/WG13. However, delays in payment of the EC contract have in turn delayed the start of the programme and data is not yet available.

3.1 Calculated measurement uncertainty

However, it is possible to calculate the measurement uncertainty from first principles, provided certain assumptions are made, using the document prepared by the ad-hoc group of uncertainty [5].

In an example specifically for benzene, document [5] (Table D.1) specifies the test parameters, procedures and criteria for assessment of measurement uncertainty. To simplify a little, the main contributions to the uncertainty budget are from the sample volume (for a pumped sampling procedure), the estimate of the mass of benzene in the sample and the mass of benzene in the blank. For a diffusive sampling procedure, the equivalent to the sample volume would be the uncertainty in the uptake rate. The other uncertainty components remain essentially the same.

Thus, for pumped sampling:

Table 1: Calculated uncertainty for pumped sampling

Parameter	Uncertainty assessment	Uncertainty contribution
Sample volume	Measurement traceable to SI, $w < 3$ % Calibration before and after sampling: difference of flows corrected to STP at start and end < 10 %	$w_{flow} < \sqrt{(3^2 + 10^2/12)} = 4.2$ %
Mass of benzene in sample	Sum of contributions from stability, recovery, calibration standards, calibration function, interferences	< 7.9 %
Mass of benzene in blank	Blank < 5 % of mass of benzene corresponding to mass sampled at limit value*	< 5 % at limit value

w = relative standard uncertainty

* in the current tests conducted by NPL, < 1 % is more reasonable

And for diffusive sampling:

Table 2 Calculated uncertainty for diffusive sampling

Parameter	**Uncertainty assessment**	**Uncertainty contribution**
Uptake rate as function of concentration	According to prEN 13528-2 [6], test 7.5: Standard uncertainty of replicates, w < 3 % Difference of mean uptake rate at extremes of environmental conditions < 20 %	$w_{diff} < \sqrt{(3^2 + 20^2/12)} = 6.5\%$
Mass of benzene in sample	Sum of contributions from stability, recovery, calibration standards, calibration function, interferences	< 7.9 %
Mass of benzene in blank	Blank < 5 % of mass of benzene corresponding to mass sampled at limit value	< 5 % at limit value

w = relative standard uncertainty

This translates into the following relative standard uncertainties of measurements by the two procedures, according to the sampled concentration:

Table 3

Concentration level	**Diffusive method**	**Pumped method**
5 µg/m^3 (1 x proposed LV for 2010)	< 11.4 %	< 9.0 %
2 µg/m^3 (40% of LV)	< 16.1 %	< 9.3 %
1 µg/m^3	< 27 %	< 10.2 %

Or as an expanded uncertainty:

Table 4

Concentration level	**Diffusive method**	**Pumped method**
5 µg/m^3 (1 x proposed LV for 2010)	< 22 %	< 18 %
2 µg/m^3 (40% of LV)	< 32 %	< 19 %
1 µg/m^3	< 54 %	< 20 %

3.2 Empirical measurement uncertainty

The calculated uncertainty may be confirmed by estimating part of the uncertainty budget from the paired results in the pilot study.

Appendix 1 gives tables of the “raw” data of means of measurement pairs, corrected for the blank value, and the calculated relative standard uncertainty, w, of each pair, as a percentage of the mean of that pair.

Summary statistics are as follows:

Table 5

Site	**Mean Concentration in ppb**	**Mean Concentration in µg/m^3**	**Mean w**	**Expanded uncertainty**
Edinburgh	0.42	1.3	7 %	14 %
Cardiff	0.58	1.9	4.4 %	8.8 %
Harwell	0.30	1.0	17 %	34 %
Marylebone	1.74	5.58	7 %	14 %

To these values should be added an estimate of the uncertainty due to the estimation in the diffusive uptake rate, w = 6.5 % (Table 2). The combined uncertainties can then be compared to the requirements of the Benzene Daughter Directive [7]:

Table 6

Site	**Mean Concentration in µg/m^3**	**Expanded uncertainty from Table 5**	**Total uncertainty**	**Target**
Edinburgh	1.3	14 %	19 %	50 %
Cardiff	1.9	8.8 %	16 %	30 %
Harwell	1.0	34 %	36 %	50 %
Marylebone	5.58	14 %	19 %	25 %

Thus, all measurements are within the requirements of the Benzene Directive as regards measurement uncertainty.

With the exception of Harwell, they are also within the requirements of the DETR guidance [2], which assumes that the criteria for indicative measurements apply. It is argued in this report that the appropriate criteria for mandatory, indicative or modelling/objective estimation should be applied, depending on the measuring range of the site.

The manual pumped method is also likely to meet these requirements, and with lower uncertainties (Table 3), but at the extra cost of manufacture and maintenance of the sampling apparatus.

3.3 Supporting data from HSE/CAR/WG5

WG5 (The personal samplers users group) of the Health and Safety Executive Committee on Analytical Requirements has undertaken a study of measurement uncertainty of Perkin-Elmer thermal desorption tubes. In this study, benzene, toluene and xylene were loaded at levels of about 50 ng each using four different laboratories (including HSL), each using a different loading procedure:

- Long-term diffusive sampling from traceable gas mixture (lower concentration);
- Pumped sampling from traceable gas mixture;
- Short-term (8-hr) diffusive sampling from traceable gas mixture (higher concentration);
- Liquid spiking.

The results were then analysed by four different laboratories (including HSL and NPL), using their own operating and calibration procedures.

The results have not yet been fully evaluated, and are presently confidential, but it is anticipated that no significant differences will be found in the results with respect to the loading techniques, the analytical laboratories or the three aromatic hydrocarbons.

In these tests, the loading errors have been kept to a minimum, so that the observed uncertainties can be attributed mainly to the analysis stage. It is anticipated that the uncertainty of the analysis will be about 2.5 % under repeatability conditions and about 3.5 % under reproducibility conditions (expressed as relative standard uncertainties). These figures suggest that the uncertainties attributed to the mass of benzene in the sample in Tables 1 and 2 are generous.

4. Data Capture

The Benzene Daughter Directive also requires > 90 % data capture for fixed measurements (mandatory measurements above 70% of the limit value) and for indicative measurements (between 40 % and 70 % of the limit value). 100 % data capture was obtained for all benzene diffusive sampling tubes exposed so far in the pilot study.

5. Time Coverage

The Benzene Daughter Directive also requires > 35 % time coverage (with some caveats) for fixed measurements (mandatory measurements above 70% of the limit value) and > 14 % time coverage (with some explanation) for indicative measurements (between 40 % and 70 % of the limit value). 100 % time coverage was obtained for all benzene diffusive sampling tubes exposed so far in the pilot study, although in one case (Marylebone, month 1) two sets of tubes were exposed for 2 weeks (rather then one set for one month) in error. This error is likely to be repeated by Edinburgh in month 8, and is likely to be caused by confusion with the two-week sampling period of the pumped tubes and butadiene diffusive samplers operated by NPL. Nevertheless, the data quality objectives have not been significantly compromised.

6. Quality assurance and Quality Control

6.1 External Quality Assurance – WASP Scheme

The HSL mean results in the ***WASP*** Proficiency Testing scheme (BTX environmental on Tenax) during the pilot study (rounds 47-49) expressed as a ratio of the standardised results ! s.d. are as follows:

Round	47	48	49
Benzene	0.96 ! .01	0.95 ! .01	0.96 ! .02
Toluene	0.99 ! .01	1.01 ! .02	1.00 ! .01
m-Xylene	1.02 ! .01	0.98 ! .02	1.02 ! .01

Thus, during the period of the pilot study, HSL has consistently achieved Category 1 status in the WASP Proficiency Testing scheme for this type of analysis.

6.2 Quality Check on Sample Tubes

The estimates of measurement uncertainty, which have been determined in section 2, enable a check to be made on the reliability of individual paired results.

Thus on the basis of results at or near the limit value (typical of Marylebone), the maximum allowable measurement uncertainty is 50 %. Taking the uncertainty component due to the uptake rate determination to be a standard uncertainty of 6.5 % (Table 2), this means that the residual standard uncertainty reflected in the pairs of duplicate results should be a maximum of 10.6 %. Thus, at a 95 % confidence level, pairs with a relative standard uncertainty of greater than 21 % should be rejected.

Similarly:

Table 7

Concentration level	Typical site	Rejection relative standard uncertainty
Above 70 % of LV	Marylebone	21 %
Between 40 % and 70 % of LV	Cardiff just below 40%	27 %
Below 40 % of LV	Edinburgh, Harwell	48 %

On this basis, none of the data pairs was rejected. However, three measurement pairs are close to the rejection values, and it is recommended that pairs where the relative standard uncertainties are half the rejection values are reviewed as in the following examples.

In the pilot study so far, there are three such values; two for Harwell (month 1 and 5) and one for Marylebone (month 6).

Table 8
HARWELL
Parts Per
Billion

		Benzene	Toluene	Ethyl- benzene	o/m/p-Xylene

Y1 M1	mean	0.39	0.44	0.08	0.30
	sd	0.11	0.04	0.03	0.01
	%cv	29%	8%	31%	2%

Table 9
HARWELL
Parts Per Billion

		Benzene	Toluene	Ethyl- benzene	o/m/p-Xylene
Y1 M5	mean	0.27	0.30	0.04	0.19
	sd	0.11	0.08	0.01	0.06
	%cv	42%	28%	20%	30%

Table 10
MARYLEBONE
Parts Per Billion

		Benzene	Toluene	Ethyl- benzene	o/m/p-Xylene
Y1 M6	mean	1.10	4.17	0.63	3.13
	sd	0.21	0.13	0.02	0.04
	%cv	19%	3%	3%	1%

In the cases of Harwell (M1) and Marylebone (M6), the results for the higher hydrocarbons are fairly consistent, suggesting that the difference in the benzene results is significant benzene blank on one of the tubes. Both tubes would in any case be checked for the blank level before re-use, so no further QC is needed.

In the case of Harwell (M5), all the results for one tube are consistently higher than the results for the other tube, suggesting a tube problem. Such tubes should be re-checked for the integrity and position of the gauze defining the length of the air gap and repacked.

7. Recommendations for Year 2/3

On the basis of the pilot study, HSL believes that the promised deliverables have been met and that the diffusive sampling method for benzene meets the requirements of the Ambient Air Directive. Depending on the ambient concentration level, the diffusive sampling method is appropriate for mandatory, indicative and modelling/objective estimation, and meets the measurement uncertainty and other Data Quality Objectives for each of these measurement tasks.

It is therefore recommended that the network of sites be expanded according to the terms of the HSL subcontract schedule 1 to Contract S009801, section 2.2.

A detail that is not covered by the current sub-contract is the provision of shelters for the exposure of the diffusive tubes on site. In the pilot study, use has been made of “nest-boxes” supplied by NPL for parallel studies on diffusive sampling of 1,3-butadiene. For the main study, there are three options:

- Continue to use boxes supplied by NPL;
- Use boxes supplied by HSL but at additional cost;
- Use inverted plastic funnels as in the original HSL validation of the benzene diffusive method [8], at no extra cost.

For the second option, boxes would probably be fabricated in aluminium. It is understood that the present boxes were originally made of wood by BP International, Sunbury, but have been in use long enough for traces of any off-gassing organic volatiles from the wood or glue to have been dispersed.

8. References

[1] Health and Safety Laboratory. The UK Ambient Hydrocarbon Air Quality Network. BTEX Diffusive Sampling. A diffusion tube handling guide for LSOs. (issued November 2000).

[2] Department of the Environment, Transport and the Regions. Review and Assessment: Monitoring Air Quality (published on website, 21 June 2000).

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[4] Brown R.H. Environmental use of diffusive samplers: evaluation of reliable diffusive uptake rates for BTX. Environmental Monitoring, **1**, 115-116 (1999).

[5] Comité Européen de Normalisation. Air Quality – Approach to uncertainty estimation for ambient air reference methods. CEN/TC264/AHG Uncertainty N 12. (issued April, 2001 and ratified by CEN TC264 May 2001).

[6] Comité Européen de Normalisation. Ambient Air Quality – Diffusive samplers for the determination of concentrations of gases and vapours – Requirements and test methods – Part 2: Specific requirements and test methods. PrEN 13528-2 (January 2001).

[7] Directive 2000/69/EC of 16 November 2000.

[8] Plant N.T., Wright, M.D. and Brown R.H. European Diffusive Sampling Initiative: Final Project Report. OMS/99/08 1999. *Available from HSL.*

Appendix 1: Means and standard deviations of measurement pairs by site and by month.

EDINBURGH

Parts Per Billion

		Benzene	Toluene	Ethyl- benzene	o/m/p-Xylene
Y1 M1	mean	0.45	1.48	0.21	0.98
	sd	0.06	0.03	0.01	0.00
	%cv	14%	2%	6%	0%
Y1 M2	mean	0.56	1.90	0.24	1.14
	sd	0.03	0.03	0.01	0.04
	%cv	5%	1%	3%	3%
Y1 M3	mean	0.61	2.17	0.31	1.45
	sd	0.01	0.03	0.01	0.01
	%cv	2%	1%	2%	0%
Y1 M4	mean	0.46	1.20	0.17	0.81
	sd	0.02	0.01	0.01	0.06
	%cv	5%	1%	8%	7%
Y1 M5	mean	0.41	1.02	0.14	0.67
	sd	0.04	0.01	0.01	0.01
	%cv	9%	1%	5%	1%
Y1 M6	mean	0.27	0.71	0.09	0.52
	sd	0.00	0.04	0.00	0.03
	%cv	0%	5%	0%	5%
Y1 M7	mean	0.21	0.70	0.10	0.50
	sd	0.01	0.01	0.01	0.01
	%cv	7%	1%	7%	3%

CARDIFF
Parts Per Billion

		Benzene	**Toluene**	**Ethyl- benzene**	**o/m/p-Xylene**
Y1 M1	mean	0.54	1.45	0.23	1.15
	sd	0.02	0.00	0.00	0.02
	%cv	4%	0%	0%	2%
Y1 M2	mean	0.77	1.84	0.27	1.40
	sd	0.05	0.04	0.01	0.01
	%cv	6%	2%	3%	1%
Y1 M3	mean	0.81	2.14	0.33	1.61
	sd	0.02	0.02	0.02	0.05
	%cv	3%	1%	7%	3%
Y1 M4	mean	0.65	1.73	0.28	1.35
	sd	0.04	0.10	0.01	0.08
	%cv	7%	6%	5%	6%
Y1 M5	mean	0.52	1.35	0.22	0.99
	sd	0.02	0.03	0.00	0.06
	%cv	4%	2%	0%	6%
Y1 M6	mean	0.39	1.06	0.15	0.76
	sd	0.03	0.01	0.00	0.00
	%cv	7%	1%	0%	0%
Y1 M7	mean	0.38	1.16	0.17	0.80
	sd	0.00	0.08	0.01	0.04
	%cv	0%	7%	4%	4%

HARWELL

Parts Per Billion

		Benzene	Toluene	Ethyl- benzene	o/m/p-Xylene
Y1 M1	mean	0.39	0.44	0.08	0.30
	sd	0.11	0.04	0.03	0.01
	%cv	29%	8%	31%	2%
Y1 M2	mean	0.44	0.71	0.11	0.45
	sd	0.00	0.01	0.01	0.03
	%cv	0%	1%	7%	6%
Y1 M3	mean	0.42	0.61	0.09	0.36
	sd	0.04	0.16	0.01	0.06
	%cv	10%	26%	8%	16%
Y1 M4	mean	0.28	0.44	0.07	0.26
	sd	0.01	0.01	0.00	0.01
	%cv	3%	3%	0%	3%
Y1 M5	mean	0.27	0.30	0.04	0.19
	sd	0.11	0.08	0.01	0.06
	%cv	42%	28%	20%	30%
Y1 M6	mean	0.16	0.15	0.01	0.12
	sd	0.03	0.01	0.00	0.01
	%cv	18%	5%	0%	6%
Y1 M7	mean	0.16	0.30	0.04	0.18
	sd	0.03	0.01	0.00	0.01
	%cv	18%	2%	0%	8%

MARYLEBONE

Parts Per Billion

		Benzene	Toluene	Ethyl- benzene	o/m/p-Xylene
Y1 M1	mean	2.57	9.46	1.42	7.07
	sd	0.12	0.17	0.04	0.22
	%cv	5%	2%	3%	3%
Y1 M2	mean	1.71	5.66	0.81	4.23
	sd	0.13	0.23	0.00	0.06
	%cv	8%	4%	0%	1%
Y1 M3	mean	2.05	6.84	0.98	4.87
	sd	0.04	0.18	0.05	0.22
	%cv	2%	3%	5%	5%
Y1 M4	mean	1.54	5.34	0.86	4.13
	sd	0.02	0.32	0.01	0.25
	%cv	1%	6%	2%	6%
Y1 M5	mean	1.78	6.00	0.91	4.47
	sd	0.13	0.13	0.06	0.10
	%cv	7%	2%	7%	2%
Y1 M6	mean	1.10	4.17	0.63	3.13
	sd	0.21	0.13	0.02	0.04
	%cv	19%	3%	3%	1%
Y1 M7	mean	1.46	5.53	0.80	4.16
	sd	0.12	0.21	0.04	0.13
	%cv	8%	4%	5%	3%

ANNEX 3 BENZENE DATA COLLECTED BY HSL DIFFUSION METHOD

Site	Start Date	Tube A PPB	Tube B PPB	spread %	Average PPB	Automatic Benzene PPB	% difference from auto
Cardiff							
	21/11/00	0.57	0.54	5.41	0.56	0.59	-5.93
	20/12/00	0.75	0.82	8.92	0.79	0.72	9.03
	17/01/01	0.81	0.84	3.64	0.83	0.81	1.60
	14/02/01	0.70	0.64	8.96	0.67	0.70	-4.69
	14/03/01	0.57	0.54	5.41	0.56	0.52	6.73
	11/04/01	0.38	0.42	10.00	0.40	0.38	5.26
	09/05/01	0.39	0.39	0.00	0.39	0.41	-4.88
	04/07/01	0.33	0.31	6.25	0.32	0.46	-30.43
	01/08/01	0.33	0.29	12.90	0.31	0.44	-29.55
	29/08/01	0.42	0.39	7.41	0.41	0.42	-4.03
	26/09/01	0.42	0.36	15.38	0.39	0.48	-17.89
	24/10/01	0.63	0.67	6.15	0.65	0.78	-16.56
	21/11/01	0.67	0.63	6.15	0.65	0.82	-20.92
Edinburgh							
	23/11/00	0.51	0.42	19.35	0.47	0.33	40.91
	20/12/00	0.61	0.57	6.78	0.59	0.68	-13.24
	17/01/01	0.62	0.60	3.28	0.61	0.67	-8.82
	14/02/01	0.47	0.50	6.19	0.49	0.45	7.30
	14/03/01	0.40	0.45	11.76	0.43	0.42	1.19
	11/04/01	0.29	0.29	0.00	0.29	0.33	-12.12
	09/05/01	0.19	0.21	10.00	0.20	0.42	-52.38
	04/07/01	0.27	0.25	7.69	0.26	0.45	-42.35
	01/08/01	0.26	0.27	3.77	0.27	0.44	-39.50
	29/08/01	0.25	0.27	7.69	0.26	0.36	-28.37
	26/09/01	0.30	0.33	9.52	0.32	0.44	-27.59
	24/10/01	0.23	0.25	8.33	0.24	0.34	-30.23
	05/12/01	1.01	0.92	9.33	0.97	1.29	-24.96
Harwell							
	24/11/00	0.33	0.49	39.02	0.41	0.18	127.78
	20/12/00	0.46	0.46	0.00	0.46	0.38	21.05

Site	Start Date	Tube A PPB	Tube B PPB	spread %	Average PPB	Automatic Benzene PPB	% difference from auto
	18/01/01	0.47	0.41	13.64	0.44	0.30	48.15
	15/02/01	0.30	0.29	3.39	0.30	0.28	6.88
	15/03/01	0.25	0.41	48.48	0.33	0.22	50.00
	11/04/01	0.20	0.16	22.22	0.18	0.13	38.46
	10/05/01	0.20	0.16	22.22	0.18	0.27	-33.33
	05/07/01	0.15	0.14	6.90	0.15	0.20	-27.50
	02/08/01	0.17	0.12	34.48	0.15	0.12	21.85
	29/08/01	0.25	0.12	70.27	0.19	0.11	72.90
	27/09/01	0.14	0.13	7.41	0.14	0.12	13.45
	26/10/01	0.23	0.25	8.33	0.24	0.18	36.36
	22/11/01	0.34	0.31	9.23	0.33	0.35	-6.07
Marylebone Road							
	22/11/00	2.39	2.79	15.44	2.59	2.46	5.28
	06/12/00	2.62	2.57	1.93	2.60	2.10	23.57
	20/12/00	1.82	1.63	11.01	1.73	1.41	22.34
	17/01/01	2.03	2.08	2.43	2.06	1.85	11.02
	14/02/01	1.57	1.54	1.93	1.56	1.29	21.01
	14/03/01	1.72	1.90	9.94	1.81	1.89	-4.23
	11/04/01	0.96	1.26	27.03	1.11	1.01	9.90
	09/05/01	1.38	1.55	11.60	1.47	1.20	22.08
	04/07/01	1.49	1.63	8.97	1.56	1.56	0.06
	01/08/01	1.48	1.62	9.03	1.55	1.66	-6.63
	29/08/01	1.15	1.19	3.42	1.17	1.15	1.92
	26/09/01	1.93	1.87	3.16	1.90	2.78	-31.70
	24/10/01	1.59	1.78	11.28	1.69	2.33	-27.71
	21/11/01	1.47	1.37	7.04	1.42	1.88	-24.63

ANNEX 4 LOCAL SITE OPERATOR MANUAL FOR NON-AUTOMATIC HYDROCARBON NETWORK

UK Non-Automatic Hydrocarbon Network

NPL Pumped Tubes and Diffusion Tubes

Local Site Operator Instructions

Issue 2 Nov 2001

CONTENTS

Issued by NPL November 2001

1 Summary of Fortnightly Procedure

1.1 Fortnightly kit

Each fortnight you will receive a package containing

A plastic travel case containing:

a) 2 diffusion tubes for benzene
c) 2 pumped tubes for benzene
d) 3 travelling blanks
e) 1 record sheet

and

f) Return packaging

The 3 types of tube contain different sorbent materials, and must not be confused. If the tubes become mixed up refer to Section 2.2 for further information

1.2 Diffusion Tubes

1) Remove the lid from the birdbox.

2) Remove the two existing 1,3-butadiene and two existing NPL benzene tubes from the birdbox by twisting off the diffusive endcaps, and removing the tubes from the top of the box.

3) Remove the endcap with the sticker from the two new 1,3-butadiene and two new benzene tubes using the CapLok tool or a pair of spanners.

4) Note the time and date on the old record sheet provided, using GMT convention.

5) Place the swagelok endcaps on the old tubes hand-tight with the CapLok tool.

6) Place the new tubes through the top of the birdbox in the marked locations, and apply the correct diffusive cap to the bottom of the tube using a twisting motion. The benzene caps have an X engraved on the side.

7) Replace the lid of the birdbox.

8) Note the time and date on the new record sheet

1.3 Pumped Tubes

1) Prepare the two new tubes by removing the swagelok endcaps with the CapLok tool or using a pair of spanners.
2) Check that the ‘Health Light’ on top of the pump box is flashing. If not contact NPL.
3) Note the time, date and the value on the hour counter on the old record sheet.
4) Slacken the lower thumb nuts and remove Tube A by lifting vertically.
5) Slacken the thumb nuts on Tube A and remove the elbow fittings.
6) Place the swagelok endcaps from a new tube on Tube A and tighten with the CapLok tool.
7) Push the elbow fittings on the new Tube A but do not tighten yet.
8) Place the new tube on the fittings on top of the box, ensuring that the engraved ring(s) on the tube are on the right hand side, and tighten all four thumb nuts.
9) Note the time, date and hour counter on the new record sheet.
10) Repeat 4 to 8 above for Tube B.
11) Check that the ‘Health Light’ is flashing. If not contact NPL.

1.4 Travelling blanks

Keep the travelling blanks (and the record sheet) in the travel case for the duration of the exposure. This should be indoors, and should be away from possible sources of hydrocarbons such as felt tip or solvent based pens.

1.5 Return packaging

The Jiffy bag provided should be used to return:

a) the 6 exposed tubes

b) the 3 travelling blanks which accompanied them, and

c) their record sheet

in the travel case as soon as possible.
If you have any questions, please contact David Butterfield on 020 8943 6391.

2 Further details with illustrations

2.1 Bird Box

The birdbox is a simple construction designed to house the diffusion tubes, in a manner that protects the tubes from rain and allows easy access, without encouraging undue attention from passers-by. It should be mounted in a position agreed by NPL, close to any existing sampling point.

Fig 2.1(a) Closed bird box

Fig 2.1(b) Open bird box

2.2 Diffusion tubes

Figure 2.2(a): Capped benzene and 1,3-butadiene diffusion tubes

1,3-Butadiene tubes will usually have a serial number starting with BN- engraved on the side, and their diffusive end caps are plain;

Benzene tubes will usually have a serial number starting with CRS-; their diffusive end caps have an ‘X’ engraved on the side.

The tubes for pumped benzene sampling will usually have a serial number starting CX-.
Refer to the record sheet if in doubt.
One spare of each diffusive cap is provided for potential future use.

Note that the correct type of diffusive end cap must be used with each type of tube.

Open the four diffusion tubes by removing the swagelok cap that has a sticker on it, using the CapLok tool or two spanners. This end also has the two grooved rings, one of which is just visible with the swagelok cap in place. Minimal effort should be required as the caps should be little more than hand-tight.

Fig 2.2(b) Uncapped diffusion tube

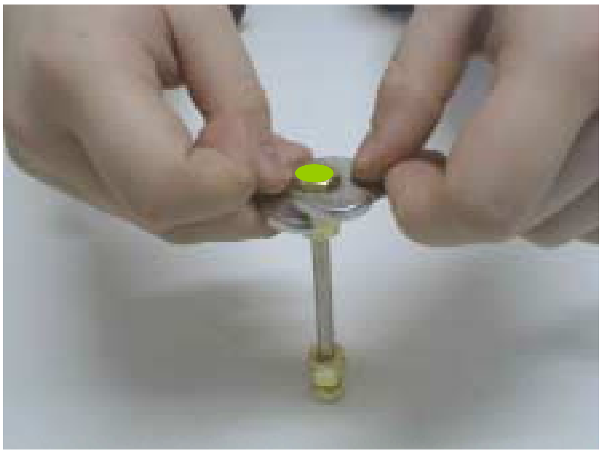


Fig 2.2(c) Opening a diffusion tube

PLEASE NOTE THAT THE STICKER CONVENTION IS OPPOSITE TO THE HSL MONTHLY BENZENE TUBES. The HSL tubes will have their stickers visible when looked at in the box; the NPL tubes will not.

2.3 Diffusion tube placement.

To minimise the potential for mix-ups, it is recommended that the holes in the bird box are always used for the same types of tube, and the positions in the box are marked accordingly using a ballpoint pen or pencil only.

Place the tubes through the holes underneath the lid of the ‘bird box’ and push the correct diffusive end caps on the open ends of the tubes (underneath the box) with a twisting motion to ensure that the seal in the cap seats correctly on the groove. Replace the lid of the box.

Note that the Benzene tubes have in this illustration been placed together in the left pair of holes.

2.4 Recording of tube details

NPL will record which tubes have been sent to you, and when they were posted.

Mark on the record sheet the exact time and date of deployment and similarly when you re-cap the tubes. The serial numbers of the tubes will be given on the sheet for reference.

Try to keep the exposure period as close as possible to two weeks.

ONLY USE BALL POINT PENS. Solvent based pens may invalidate the measurement.

2.5 Replacement of tubes

After two weeks of exposure, remove the tubes from the birdbox by twisting off the diffusion cap. Place the swagelok caps from the next tubes on the old tubes and tighten using the CapLok tool. It should not be possible to use excessive force. However, if spanners must be used, only use ¼ turn beyond hand tight. Excessive force will deform the tube and may render the tube useless and the measurement invalid. See Fig 2.2(c) above showing minimum leverage being used.

Note the time and date on the record sheet, and deploy the next set of tubes as above, re-using the correct diffusive end-caps.

2.6 Return of tubes

Place the exposed tubes and the travelling blanks in the packaging provided along with the pumped tubes (see below) and record sheet and return to NPL as soon as possible.

2.7 NPL Controlled flow pumped tube sampler

This will be installed by NPL staff in a suitable location, close to mains power and a convenient sampling point. It consists of a wall or desk mounted metal box to which the pumped tubes are connected, and a floor mounted pump. Care should be taken not to kick or knock the pump, which will normally be on the floor directly below the box.

The two tubes on the pump box are to be replaced every fortnight, normally to coincide with changing the diffusion tubes.

2.8 Preparation of pumped tubes

The tubes for pumped benzene sampling will usually have a serial number starting CX-. The end nuts will not have a sticker on either end.

Remove the swagelok nuts from BOTH ends of the two pumped tubes using the CapLok tool or a pair of spanners. You may find it useful to remove the end with the grooved rings first as sometimes the PTFE olive can ‘flow’ into the ring, making removal slightly difficult.

2.9 Removal of old tubes from the pump box

Ensure that the ‘health’ indicator is flashing. If not contact NPL immediately. Otherwise, make a note of the time, date, and the reading on the hour counter in front of the tubes, in the space on the sheet provided.

Record the sample bypass flow from the rotameter, located inside the sampler. The flow reading should be read from the top of the ball and the indicated flow recorded on the sample record sheet.

Slacken the lower thumb nuts of tube A and lift the tube and the elbow fittings off the box. Slacken the thumb nuts on the tubes and remove the fittings. Apply the swagelok caps from the new tubes and tighten using the CapLok tool.

2.10 Installation of new tubes on the pump box

Fig 2.10(a) Installation of a new tube Fig 2.10(b) New tubes in place

Push the elbow fittings on the new Tube A. The elbow fittings can be used either way around. DO NOT TIGHTEN AT THIS TIME.

Ensuring that the engraved rings on the tube on the right hand side, place the tube and fittings over the uprights for Tube A and push down. Hand tighten all four thumb nuts once the tube is securely in place. Make a note of the time, date and hour counter on the new record sheet. Remove and replace tube B in the same manner.

2.11 Return of tubes

Place the exposed tubes, travelling blanks and record sheet in the travel case along with the diffusion tubes and return to NPL as soon as possible in the Jiffy bag provided.

For reference, the address on the adhesive label is:

David Butterfield / Duty Officer
NPL
FREEPOST PHQ9
B95, Rm257
Queens Road
TEDDINGTON
Middlesex
TW11 8BR

Please note that this address should be used for the return of tubes only. All other correspondence should be addressed as given in Section 3.0 below.

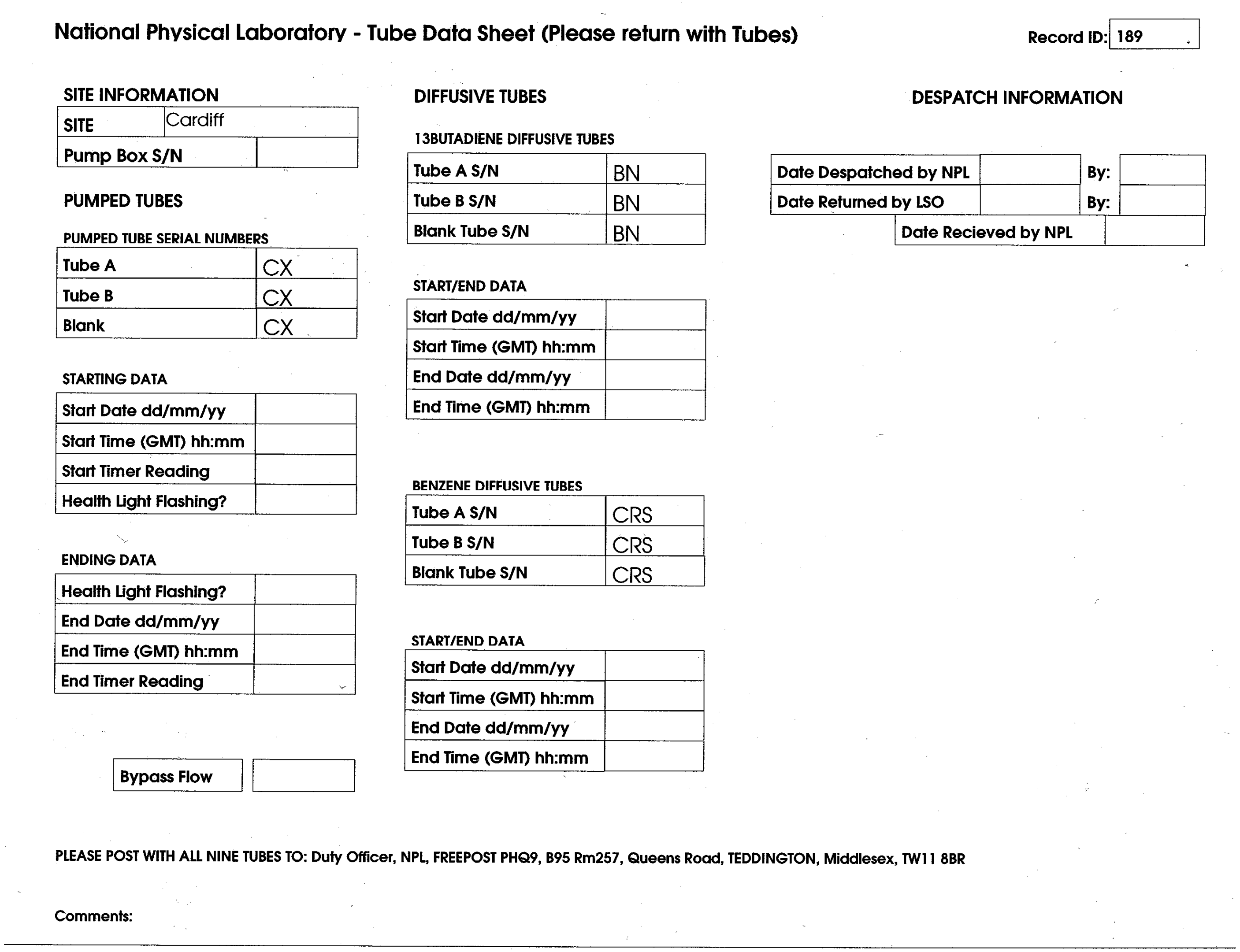
3.0 Contact details

Your main contact at NPL is

David Butterfield
NPL
Queens Road
Teddington
Middlesex
TW11 0LW

Tel: 020 8943 6391
Fax: 020 8977 4591
Email: david.butterfield@npl.co.uk

4.0 Sample Record Sheet



National Physical Laboratory - Tube Data Sheet (Please return with Tubes)

Record ID: 189

SITE INFORMATION

SITE	Cardiff
Pump Box S/N	

PUMPED TUBES

PUMPED TUBE SERIAL NUMBERS

Tube A	CX
Tube B	CX
Blank	CX

STARTING DATA

Start Date dd/mm/yy	
Start Time (GMT) hh:mm	
Start Timer Reading	
Health Light Flashing?	

ENDING DATA

Health Light Flashing?	
End Date dd/mm/yy	
End Time (GMT) hh:mm	
End Timer Reading	

Bypass Flow	

DIFFUSIVE TUBES

13BUTADIENE DIFFUSIVE TUBES

Tube A S/N	BN
Tube B S/N	BN
Blank Tube S/N	BN

START/END DATA

Start Date dd/mm/yy	
Start Time (GMT) hh:mm	
End Date dd/mm/yy	
End Time (GMT) hh:mm	

BENZENE DIFFUSIVE TUBES

Tube A S/N	CRS
Tube B S/N	CRS
Blank Tube S/N	CRS

START/END DATA

Start Date dd/mm/yy	
Start Time (GMT) hh:mm	
End Date dd/mm/yy	
End Time (GMT) hh:mm	

DESPATCH INFORMATION

Date Despatched by NPL		By:	
Date Returned by LSO		By:	
Date Recieved by NPL			

PLEASE POST WITH ALL NINE TUBES TO: Duty Officer, NPL, FREEPOST PHQ9, B95 Rm257, Queens Road, TEDDINGTON, Middlesex, TW11 8BR

Comments: