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Report

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CPEA 28: Airborne Particulate Concentrations and Numbers in the United Kingdom (phase 2)

Annual Audit Report

Bryan Sweeney
Rachel Yardley
David Butterfield

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National Physical Laboratory | Hampton Road | Teddington | Middlesex | United Kingdom | TW11 0LW

Switchboard 020 8977 3222 | **NPL Helpline** 020 8943 6880 | **Fax** 020 8943 6458 | **www.npl.co.uk**

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of the Managing Director, NPL, by Dr S Windsor,
authorised by the Director, Quality of Life Division.

Executive Summary

The annual audit round for the Airborne Particulate Network was carried out during June 2006, 12 months after the previous audits. Their main purpose is to carry out instrument checks and calibrations so that data ratification can account for corrections for instrument drift throughout the year, and, more generally, greater confidence can be placed on the ratified data. The audits also allow for assessment of the site infrastructure and operator competence.

All instruments were operational during the audit round except for the SMPS analysers, and the automatic nitrate analyser at Belfast. The SMPS instruments had not been operational for several months due to their age and the fact that they are no longer supported by the manufacturer. Defra had been kept aware of the situation and replacement SMPS instruments are planned.

Full audits were carried out on all operational instruments. This included checking for leaks and calibrating flow rates; performing zero/blank tests; and calibration, using certified gas standards and an aqueous calibration for the automatic nitrate analysers. The audit results will be used together with the 2005 audit results to ratify the Network data.

No significant problems were found with the condensation particle counters or the daily sulphate samplers.

Both the continuous nitrate and the continuous carbon analysers give complicated results that reduce confidence in the ratified data from these instruments. These need to be investigated more fully in future work.

Some other issues that should be highlighted are:

There is an issue with safety at the new Harwell site. Access to the roof of the building is via an unstable temporary staircase and the local site operator is unable to reach the sampling heads from this staircase. NPL is working with Netcen to arrange a safe alternative.

The condensation particle counter at Birmingham is situated beneath overhanging trees. NPL will take steps to address this problem and will report to Defra at a later date.

CPEA 28: AIRBORNE PARTICULATE CONCENTRATIONS AND NUMBERS IN THE UNITED KINGDOM (PHASE 2)

Annual Audit Report

1 Introduction

In June 2005 the National Physical Laboratory (NPL), under contract to the Department of the Environment, Food and Rural Affairs (Defra), took over the running of the Airborne Particulate Concentrations and Numbers in the UK Network from Casella Stanger. An initial State of Network Report was published in September 2005. One year after the start of the contract, the audit of instruments and Local Site Operators (LSOs) has been repeated.

Annual audits play an important role in the quality procedures of air quality measurements. The audit round has three objectives:

1. To assess the site infrastructure in terms of safety, accessibility and compliance with CEN siting requirements for air quality monitoring.
2. To ensure the LSO is properly trained and competent in carrying out routine cleaning and maintenance procedures.
3. To carry out calibration of the instruments and provide traceability to national standards, and other operational tests. This information is used during the ratification process to apply corrections to the data, ensuring intercomparability of data at each monitoring site and greater overall confidence in the data.

1.1 Instrument Availability

The following table details the dates of the audits and the overall status of the analysers at each site during the audit.

Table 1.

Site	Date of Audit	CPC	SMPS	Automatic Carbon	Automatic Nitrate	Daily Sulphate
Harwell	22/6/06	-	n/w	ok	ok	ok
Birmingham	26/6/06	ok	-	-	-	-
Manchester	26/6/06	ok	-	-	-	-
Marylebone Road	20/6/06	ok	n/w	ok	ok	ok
North Kensington	21/6/06	ok	-	ok	-	ok
Bloomsbury	n/a	-	n/w	-	-	-
Glasgow	28/6/06	ok	-	-	-	-
Belfast	27/6/06	ok	-	ok	n/w	ok
Port Talbot	23/6/06	ok	-	-	-	-

Ok The analyser was in a condition that allowed the audit checks to be carried out.

n/w The analyser was at the site but was, for whatever reason, not operational.

- This analyser type was not installed at the site.

2 Condensation Particle Counters (CPC)

It is not possible, at present, to inject a known and traceable number of particles into this analyser type, in-situ, which would act as a calibration for the analyser. All that may be done to check the analyser performance is to measure the sample flow rate to the analyser, and to allow it to sample through a HEPA (high efficiency particle attenuator) filter to check the analyser zero. It was also possible to check the analyser self-diagnostics. Calibration of number calibrations is currently carried out during servicing by the Equipment Service Unit (ESU) using their in-house calibration facilities, using a particle generator and an independent "standard" particle counter.

The results of the audit checks are shown in Table 2 below.

Table 2.

Site	HEPA response (Particles/cm^3)	Sample flow (vl/min) *Set point 0.3*	Sample flow (vl/min) *Set point 1.5*	Diagnostics
Port Talbot	<0.3	0.262	1.45	Ok
Belfast	<0.1	0.276	1.45	Ok
Birmingham	<0.1	0.270	1.62	Ok
Manchester	<4.0	0.272	0.89	Ok
Glasgow	<0.2	0.260	1.69	Ok
Marylebone Rd	<0.1	0.285	1.00	Ok
North Kensington	<3.0	0.264	1.64	Ok

Measurements of both sets of flow rates at ambient conditions are given above. The uncertainty in the high flow measurements, for 95% confidence limits is +/- 3%. The uncertainty in the low flow measurements is estimated to be +/- 5%. Flows were measured using a BIOS Dry Cal flow meter, which had been recently calibrated using a Brooks volumeter.

It had been noted that there could be significant variations in analyser sensitivity immediately before and after servicing. The ESU has therefore been asked to record the results of the calibrations both before and after service, so that corrections for drift can be made with much more confidence.

It was found that some CPCs had been returned from the ESU after service in low flow mode. To reduce the effects of particle losses to the sampling system, the flow rates were changed from low flow to high flow at the audit visits. The flow rates were changed at North Kensington, Belfast, Port Talbot, Manchester, and Glasgow.

Table 2 shows large deviations from the high flow rate set point at Manchester and Marylebone Road though this is not expected to have a significant effect on the data. In high flow mode the pump draws a nominal 1.5 litres of air per minute to reduce particle deposition inside the instrument. The flow is split and 0.3 litres per minute are directed to the optical detector. The remaining 1.2 litres bypass the optics and are exhausted. It is therefore the results from the low flow measurements that are used during the data ratification process.

3 Scanning Mobility Particle Sizers (SMPS)

During this set of visits, none of the SMPS analysers were operating. Defra have been informed that the SMPS analysers are not working and are no longer supported by the manufacturer. TSI Instruments and Grimm Aerosol have provided quotes for replacement instruments.

4 Daily Sulphate Samplers

As with the CPC measurements, the only on site calibration currently possible for these samplers is to measure analyser flow rates, and perform a leak check. In addition, a check can be made on whether filters are being correctly identified within the data handling process. Quality assurance of the resulting data also requires auditing of the laboratory ion chromatography analysis, which is carried out and reported separately. The results of the volumetric flow rate measurement at ambient conditions, and leak checks on the sulphate analysers, are shown in Table 3 below.

Table 3.

Site	**Sample Flow (vl/min)** ***Set point 16.67***	**Filter in use**	**Leak test**
Harwell	16.47	p0001564	pass
Belfast	16.39	p0001592	pass
Marylebone Rd	16.09	p0001555	pass
North Kensington	16.51	p0001535	pass

The leak test is “passed” if the flow is less than 1.5 l/minute with the sample inlet “blocked off”.

The uncertainty in the flow measurements, for 95% confidence limits is +/- 3%.

A record was made of the filter number, noted from the analyser display, in use at each site during the audit. Checks have been made that the reported concentration from that particular filter has been correctly assigned to the date of the audit.

The chemical analysis for the determination of sulphate deposited on the filters is subject to laboratory QA/QC procedures. These include the following (reported separately):

1. Daily calibration of ion chromatograph traceable to primary standards
2. Regular intercomparisons with other measurement laboratories
3. Routine instrument service and maintenance
4. Analysis of blank filters
5. Development of a full uncertainty budget
6. Repeated extractions of sample filters

5 Automatic Nitrate Analysers.

More than any other instruments described in this report, the automatic nitrate analysers allow a nearly complete calibration of their full measurement system. This is done in two ways:

1. Injection of gas mixtures into the NO_x analyser to determine its response
2. Measurement of liquid nitrate solutions placed directly on the flash strip of the analyser.

Both sets of calibrations were carried out during this audit round.

5.1 Gas Calibration of Chemiluminescent NOx Analysers

Three gas standards were transported to each site. They were 5.1 ppm NO, 2.7 ppm NO with 2.3 ppm NO_2, and 8 ppm NO_2 with 0.4 ppm NO, all in a balance gas of nitrogen. These standards had been prepared gravimetrically using a calibrated balance at NPL. Their concentrations were verified by dynamic dilution techniques. Each was injected into the analyser using the audit facility in the analyser software.

Figures 1 and 2 show the results of these tests at Marylebone Road and Harwell respectively. Each graph shows the analyser response factors as a function of the ratio of NO to NO_x of the calibration standard used. Both the steady state response factor and the pulse read response factor have been plotted. As can be seen, the steady state calibration factors are reasonably constant when the NO/NO_x ratio is in the range 0.6 to 1.0. However, with more NO_2 in the cylinder, at NO/NO_x at approximately 0.1, the factors are seen to increase, showing that the analyser is less sensitive to mixtures containing higher concentrations of NO_2. This may be due to inefficiencies in the NO_2 converter at higher NO_2 concentrations. It is our understanding that the converter used in the instruments is heated molybdenum, and similar to the converter used in ambient level NO_x analysers. Other than the tests documented here, it is not known how these converters respond to high (ppm level) concentrations of NO_2.

Figure 1.

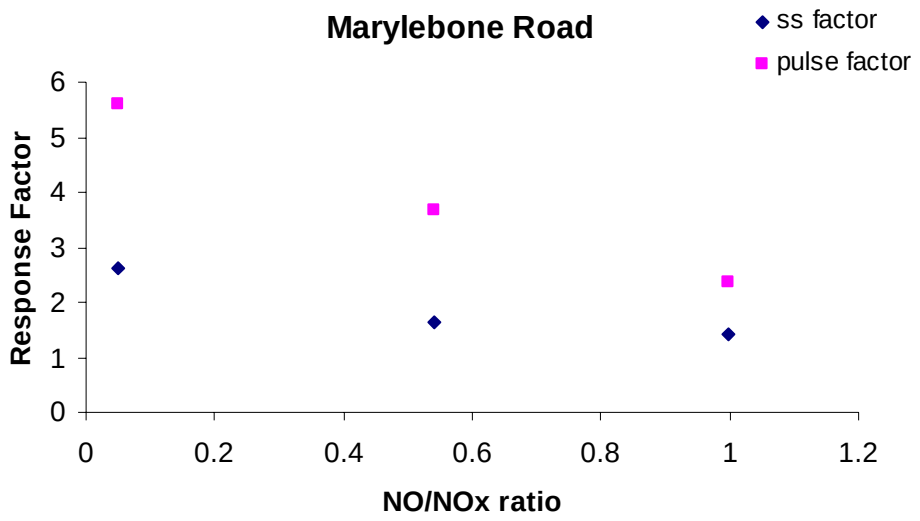
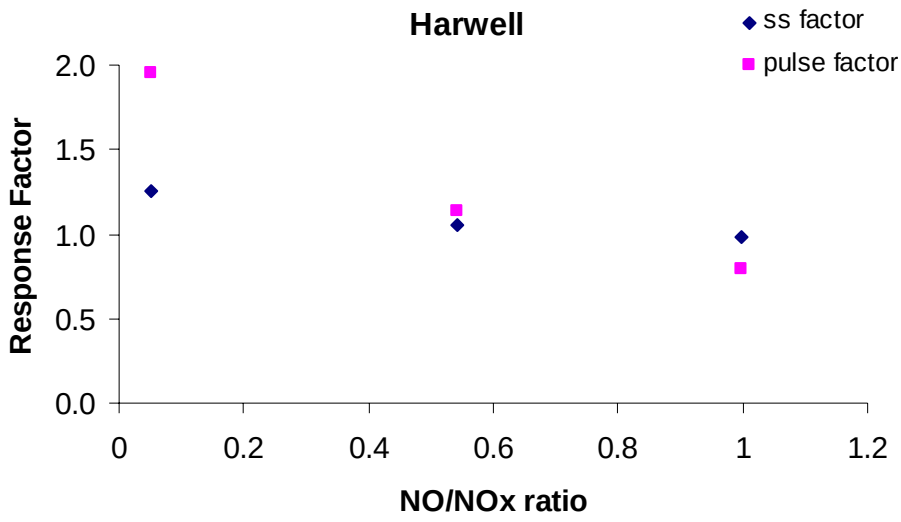


Figure 2.



It can be seen that in the pulse mode, which is more akin to normal operation, the factor varies to a larger extent depending on the NO/NO_x ratio of the standard used.

The findings from this set of audit tests are similar to the results seen in the previous audit round in 2005.

The relative proportions of NO and NO_2 produced when the analyser is in ambient measurement mode are not known. This may depend upon the relative concentrations of the particular nitrate species being sampled. Thus the effects of converter inefficiency cannot, at this stage, be reliably determined. The advice of the ESU and instrument manufacturer will be sought.

5.2 Liquid Calibration of the Automatic Nitrate Analysers

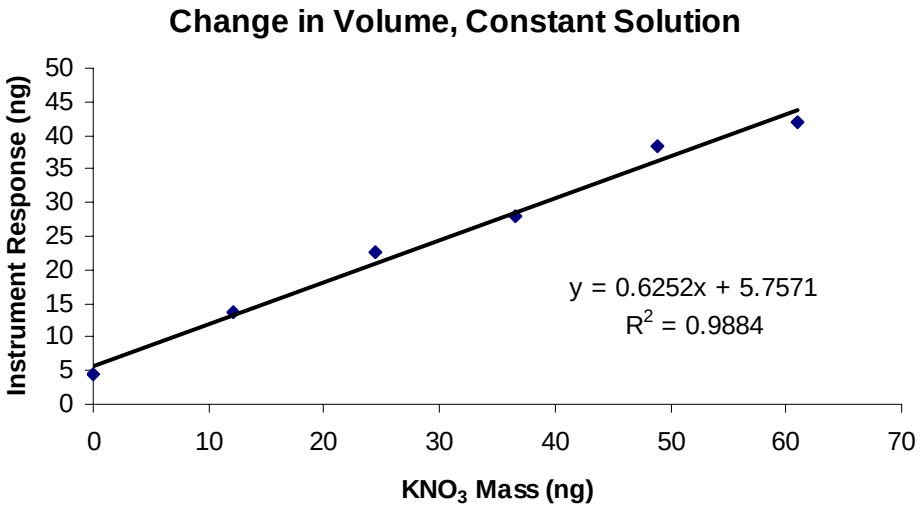
Standard solutions of potassium nitrate, KNO_3, were prepared gravimetrically at NPL. Accurately known volumes of these were injected onto the flash strip of the analyser, and the responses noted.

Known volumes of double deionised water were also injected onto the flash strip to determine the analyser zero response.

This method of calibration tests both the flash strip burning efficiency and the pulsed response of the nitrogen oxides analyser. It is likely, therefore, to lead to a more reliable overall determination of analyser response factors.

Figure 3, below, shows an example of the response factor as a function of volume of a single solution deposited on the flash strip of the Marylebone Road analyser.

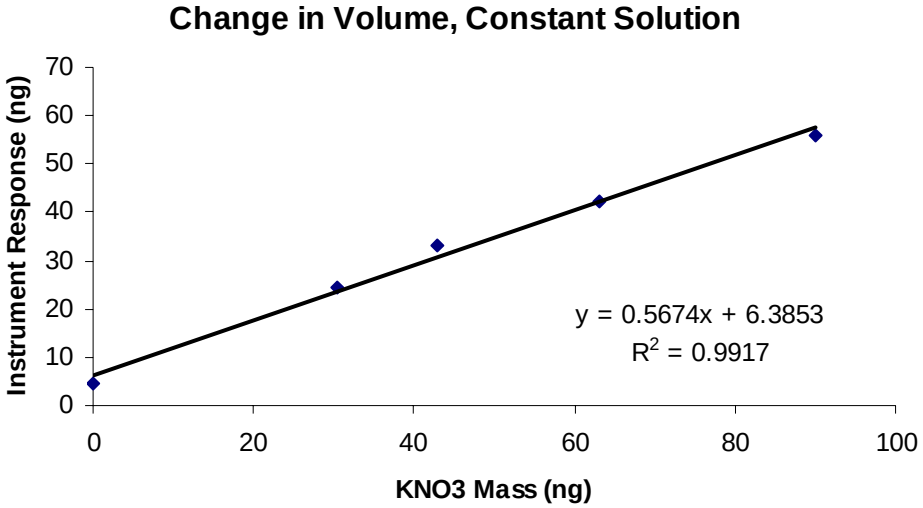
Figure 3.



As can be seen, there is a linear correlation between the amount of KNO_3 deposited and the instrument response, though will a significant zero offset.

Figure 4, below, shows the response factor as a function of concentration at a constant volume of a number of different solutions, also deposited on the flash strip of the Marylebone Road analyser.

Figure 4.



There is again a linear correlation between instrument response and concentration of solution used, with a significant zero offset.

The response factors from both sets of calibrations are tabulated below, together with the analyser zero response and standard deviation of the zero readings obtained.

Table 4 . Nitrate analyser response factors

Site	Marylebone Road	Harwell
Constant Volume		
Gradient	0.567	0.736
Zero Offset	6.385	3.647
Constant Solution		
Gradient	0.625	0.674
Zero Offset	5.757	5.047
Water response (ng)	4.4	4.0
St. Dev. of Water (ng)	0.6	0.9

These response factors will be used to scale ambient data to produce a consistent data set. It is curious to note that the offsets seen in the linear regressions and in the response to pure water are sometimes clearly absent during ambient sampling, when concentrations lower than the offset are recorded.

It was noted that large variations in analyser response were sometimes obtained when using the standard solutions. This was also the case when using the deionised water for the zero readings. The data given above have had the obviously anomalous measurements removed.

These outstanding issues with the automatic nitrate analysers will be investigated further in future.

5.3 Comparison of Liquid and Gas Calibrations of Nitrate Analysers

It is interesting to note that there are large differences in the sensitivity of the site analysers when sampling from the gas standards that are not reflected in the liquid calibrations. The table below illustrates this:

Table 5.

Site	Mean Sensitivity Liquid Calibration (Response:Actual)	Mean Sensitivity Gas Calibration (Response:Actual)	Ratio of sensitivities
Harwell	0.7	0.89	0.79
Marylebone Rd	0.6	1.89	0.32

The mean sensitivity to the liquid calibration is the mean of the values given in Table 4, whereas the mean sensitivity for the gas calibration is the mean of the steady state and pulse response factors, using the 5 ppm NO mixture, from Figures 1 and 2.

As can be seen, although both analysers have a similar response to the liquid calibration, there is a large difference in the response to the same 5 ppm NO cylinder. The reason for this is not known but may be due to an instrument malfunction. The ESU will investigate.

It is not known if this effect is significant. If the composition of ambient nitrate were primarily KNO_3, the compound used in the aqueous calibrations, application of the aqueous calibration factors would lead to a reliable data set. This is not expected to be the case, and the generation of the NO_x pulse on the analyser flash strip from ambient nitrate may produce NO_x samples with varying relative amounts of NO and NO_2. In this event, the analyser response characteristics would be more likely to follow the patterns seen with the gas calibrations. Further testing will be carried out using different nitrate solutions to perform the aqueous calibrations to determine whether KNO_3 is the most suitable nitrate for the purpose.

6 Continuous Carbon (OC/EC) Analysers

The carbon analysers operate by burning the carbon species to produce carbon dioxide, which is detected by the analyser's LiCor sensor. Varying the temperature at which the carbon species are oxidised gives a measure of organic and total carbon species, from which elemental carbon concentrations can be calculated. Unlike the automatic nitrate analyser, it is not possible to introduce test solutions directly onto the collector.

6.1 Gas Standards Calibrations

NPL calibrated the analysers using certified cylinders of 2500 ppm and 4500 ppm CO_2 in nitrogen. The results of these calibrations are given in the following table:

Table 6.

Site	Zero response	Response to 2500ppm CO_2	Deviation %	Response to 4500ppm CO_2	Deviation %
Harwell	19	2347	-8	4248	-5.0
North Kensington	276	2541	-10.6	4103	-14.1
Belfast	-110	2008	-16.4	3760	-13.1
Marylebone Rd	4	1523	-40.0	4541	+1.8

The deviations calculated above are the percentage difference between the zero corrected analyser response and the concentration of the gas standard used. As can be seen from the measured deviations, there are some significant deviations from the concentrations of the NPL standards used. Also of note is the fact that the deviations do not appear to be constant over the two concentrations of gas standards used. This is particularly true at Marylebone Road. Repeat measurements of the NPL cylinders at the sites has shown that the analysers' estimation of their concentration is, at least, reproducible, with standard deviations of repeat measurements being less than 0.2% of value in all cases. The dependence of the measured deviation on concentration may be indicative of some non-linearity in these analysers.

6.2 Flow checks on Ambient Carbon Analysers

The carbon analyser flow rates were measured with a calibrated flow meter, and the analysers were leak tested. The results of these checks are given in the table below:

Table 7.

Site	Sample flow (vl/min) *Set point 16.67*	Leak test
Marylebone Road	16.27	ok
Harwell	15.65	ok
Belfast	15.87	ok
North Kensington	16.31	ok

7 Other Issues

The CPC sample line at Glasgow had been sheared off just above the roof of the enclosure allowing rain to be drawn down the sample line. This was repaired and a rain funnel fitted to the line. It is not known what effect rain would have had on the analyser. As there is a rain jar just up-stream of the analyser, the effects may have been small.

The CPC inlet at Port Talbot, although configured in an upturned U shape, did not have a rain funnel. A rain funnel has since been sent to the LSO.

Following relocation of the analysers at Harwell, it is now very difficult to access the carbon analyser PM_{10} head for cleaning. It is not possible to walk on the roof of the site, and the temporary flight of stairs, as well as leaving a rather large gap between the top of the stairs and the top of the shelter, does not seem very stable. NPL would recommend that the bottom of the stairs be rested on an appropriate object to narrow the gap at the top, and that the top of the stairs be fixed at the top of the enclosure. NPL is working with Netcen (AEAT) to provide safe access and in the meantime the LSO has been advised not to attempt cleaning procedures on the roof.

LSO audits were carried out at Glasgow, Port Talbot and Harwell. The LSOs were seen to be carrying out their duties effectively.

The PM_{10} head on the Partisol at Harwell had been incorrectly assembled. This was rectified at the audit. It is likely that the effects of the incorrectly assembled head on the particle size distribution sampled would have been small and this only affects a very small proportion of the data. The LSO has been retrained in the cleaning and assembly of the Partisol sampling head.

The Birmingham CPC analyser, as with all other analysers at this site, are beneath overhanging trees. This does not meet CEN siting requirements and may affect the measurement. NPL will take steps to address this problem and will report to Defra at a later date.

8 Conclusions and Recommendations

All of the sites in the UK Particles Network have been audited in order to reliably determine the analysers' response factors and other relevant information. This will help ensure a consistent data set across the network.

Some aspects of analyser performance could not be determined as there is presently no way of generating traceable and reproducible particle concentrations, at the required flow rates, in the field. Also tests on, for instance, nitrate or carbon analyser sample collection efficiency have not been carried out. Without some measurement of these important aspects of the measurement process, the overall uncertainty of the measurements cannot be reliably quantified. There is clearly a need to explore robust techniques and methods for generating calibration samples for these analysers.

Tests carried out on the CPC analysers have allowed the instrument flow rates and zero responses to be determined. The zero response tests showed that the analysers gave a true zero reading, indicating that the measurement system was working well in this respect and that there were no leaks in the instruments.

Flow tests carried out on the daily sulphate analysers will allow the data to be rescaled to reflect measured flow rates. All instruments passed the leak tests.

The automatic nitrate analysers were calibrated using standard liquid solutions and aspects of analyser performance were also checked using gas calibration standards, prepared by gravimetric means at NPL. In general, the nitrate analysers showed consistent response to the liquid standards. However, in line with the previous audit, several aspects of the results are not adequately understood, and further investigation of the analyser converter efficiency and other possible effects on measured ambient concentrations should be undertaken.

The automatic carbon instruments, audited for the first time this year as they were all being serviced at the start of the contract, also show results in response to gas calibration standards that are not adequately understood, and again further investigation is required.