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Certificate of Calibration

REPORT ON THE RESULTS OF AMBIENT AIR QUALITY ANALYSER CALIBRATIONS CARRIED OUT AT NERC "SUPERSITES" IN LONDON, BIRMINGHAM AND MANCHESTER, MAY 2022.

CUSTOMER:	IMPERIAL COLLEGE LONDON UNIVERSITY OF BIRMINGHAM UNIVERSITY OF MANCHESTER
IDENTIFICATION	The instruments calibrated are identified in Table 1.
CALIBRATION PERIOD	The instruments were calibrated as shown in Table 1.
UNCERTAINTIES	The reported uncertainties are based on a standard uncertainty multiplied by a coverage factor, *k* = 2, providing a level of coverage probability of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.
VALIDITY	The results quoted here are valid on the date of measurement only. However, subject to ongoing quality assurance checks, analysers of this type are likely to remain stable, or undergo readily quantifiable drifts, for periods of up to six months.

Reference NERC 0522 bs
Date of Issue: 10th May 2022
Checked by: BS

Signed D. Butterfield
Name: D M Butterfield
(Authorised Signatory)
on behalf of NPLML

NPLC01-07/15

1 MEASUREMENT PROCEDURE

The procedure used was NPL procedure QPDQM/B/521.

1.1 Gaseous Analysers:

1.1.1 Analyser Response Factors

Stable calibration standards, validated against primary standards, are transported to each site and sampled by the analyser.

The analyser also samples from a cylinder containing certified metrology grade zero air.

The analyser factor quoted is the response to the intercalibration standard, expressed in $nmol.mol^{-1}$/logged unit, with the zero point being the response to zero air.
For ozone, the response factor is the slope of the calibration function, m, relating analyser response to NPL standard response, i.e.
Site analyser = m NPL standard + c
Thus, the units for the ozone calibration factor are logged unit/($nmol.mol^{-1}$)

For oxides of nitrogen analysers, the NO_x and NO channel response factors are derived from the NO in nitrogen cylinder.

For ozone analysers, the calibration is carried out by comparison of the analyser response with that of a calibrated ozone photometer, over a range of ozone concentrations generated by the photometer.

1.1.2 Uncertainty due to analyser linearity/repeatability effects

To determine analyser linearity/repeatability effects, a series of amount fractions are produced (using dynamic dilution techniques) covering the analyser range. The analyser output is noted for each of these amount fractions. A linear regression is then carried out, relating analyser output to the dilution factor at each point. The linearity error is defined as the maximum residual of the regression slope.

For the CAPS nitrogen dioxide analysers, linearity is measured by measuring the NO_2 produced at a range of concentrations during the converter efficiency test detailed in 1.1.4 below. A linear regression is then carried out, relating CAPS NO_2 measurement to the NO_2 measured by the chemiluminescent analyser. The linearity error is defined as the standard error of the residuals of the regression slope.

1.1.4 Converter Efficiency

Converter efficiency is determined as follows:

A stable amount fraction of NO is produced, by two stage dynamic dilution, and the analyser outputs, NO_x and NO, are noted after a suitable stabilisation period.

Ozone is added to the sample, converting some NO to NO_2, while the total NO_x in the sample remains constant. Again, following appropriate stabilisation times, the NO_x and NO outputs are noted.

Converter (in)efficiency is defined as the change in scaled NO_x signal as a percentage ratio of the change in the scaled NO signal.

1.1.5 Estimation of Site Cylinder Amount fractions

The site cylinder amount fractions are evaluated by sampling from the site cylinder and using the analyser response factors, section 2.2, to derive their amount fraction.

2 RESULTS

2.1 Analysers Calibrated

The analysers calibrated, are given in Table 1.

Table 1

Site	date	NOy analyser	NO_2 analyser	CO_2/CO and CH_4 analyser	Ozone analyser	SO_2 analyser	Particle analyser
London	6/5/2022	T200U 23419	t500u 23556	LGR 23499	T400 23555		Fidas 9378
Birmingham	5/5/2022	T200U 23450	T500u	LGR 23543	TE49i	T100U 23449	Fidas 9424
Manchester	4/5/2022	TE42iY NOy	T500U 23240	TE 48i	TE49i		Fidas 6825

2.2 Gaseous Analyser Response Factors, Uncertainties due to Linearity/repeatability, and NO_2 Converter Efficiencies.

			London	Birmingham	Manchester
Ozone		Zero response	0.0	1.0	0.2
		Response Factor	0.922	0.846*	0.915
		Linearity error	0.6	0.7	0.4
		Analyser software span coefficient	0.906	0.988	1.060
NO_y	NO_y	Zero response	3.6	-0.7	0.9
		Response Factor	1.223	1.093	1.715
		Linearity error	3.5	3.7	0.9
	NO	Zero response	2.0	-1.1	0.0
		Response Factor	1.215	1.087	1.683
		Linearity error	0.8	1.3	1.6
		Conv effy	97.4	97.9	99.5
CAPs NO_2		Zero response	0.0	2.4	0.0
		Response Factor	0.959	0.818	0.950
		Linearity error	5.5	2.4	1.2
CO		Zero response	0.04	0.03	6.12
		Response Factor	0.882	0.973	0.842
		Linearity error	0.09	0.10	0.16
LGR CH_4		Zero response	0.02	0.01	0.01
		Response Factor	0.934	1.005	0.975
		Linearity error	0.05	0.03	n/a**
LGR CO_2		Zero response	0.28	0.36	0.76
		Response Factor	0.957	0.983	0.970
		Linearity error	17.9	5.2	n/a**
SO_2		Zero response		1.5	
		Response Factor		0.874	
		Linearity error		4.8	

Data presented above, for response factor, are derived from the analyser front panel, and are thus in units of $nmol.mol^{-1}$/indicated $nmol.mol^{-1}$. (CO_2, CH_4 and CO data are in $\mu mol.mol^{-1}$/indicated $\mu mol.mol^{-1}$)
Analyser zero data are in indicated nmol/mol or indicated µmol/mol
Data on linearity error, more correctly, uncertainty due to linearity and repeatability, are in nmol/mol or µmol/mol.
Converter efficiency data are in %.

*The ozone analyser at Birmingham was displaying a "low flow" warning
** The full range of instrument tests are not carried out on the CO_2/CH_4 analyser at Manchester

2.3 Uncertainties in the Response Factors

The reported uncertainties are based on a standard uncertainty multiplied by a coverage factor, $k = 2$, providing a level of coverage probability of approximately 95%.

They are derived from uncertainties in the transfer standards used and measured drifts, and measurements of analyser zero and span noise, and uncertainty due to linearity/repeatability.

Measurand	London	Birmingham	Manchester
CO_2	3.5	3.0	n/a
CH_4	6.1	3.4	n/a
CO	3.4	3.4	2.9
NO_y	3.5	3.5	3.3
NO	3.3	3.3	3.8
NO_2	5.9	5.3	6.0
SO_2		3.9	
O_3	4.0	4.0	4.0

Uncertainties in converter efficiency are of the order of 3 to 4 % absolute.

2.4 Ranges over which the Analysers were Calibrated

The following Table list the maximum concentrations, as reported by the respective analyser, over which the analyser was tested, i.e. the range of the linearity test. These values are, therefore, the range over which the calibrations are valid.

Measurand	London	Birmingham	Manchester
CO_2(µmol/mol)	2090	2034	
CH_4(µmol/mol)	10.18	10.24	
CO(µmol/mol)	27.8	26.6	30.2
NO_y (nmol/mol)	706	681	755
NO (nmol/mol)	675	670	746
NO_2 (nmol/mol)	106	120	71
SO_2 (nmol/mol)		716	
O_3 (nmol/mol)	194	195	194

2.5 Results of FIDAS calibrations

	London	Birmingham	Manchester
flow/slm (at 273 K and 1013 mbar)	4.46	4.40	4.48
dust peak	140.02	n/a	141.28
hepa test particles/cm^3	0	0	0

2.6 Amount fraction of On-site Standards

The amount fractions of the on-site standards are given in Table 6:

		London		Birmingham		Manchester	
		ID	Conc nmol/mol	ID	Conc nmol/mol	ID	Conc nmol/mol
NO	NO_x	113321	441	112969	481	145254	453
	NO		440		480		
NO_2		d360296	364	112367	455		
SO_2				D116860	372		
CO						293878	4.99*

*Units are µmol/mol

The uncertainties in the site standard measurements are ±5% of value.

3 Accreditation to ISO 17025

NPL is currently accredited to ISO 17025, often referred to as UKAS accreditation, for calibration of Nitrogen Oxides, Ozone, Carbon Monoxide, and Sulphur Dioxide analysers, the on-site calibration standards relating to these analysers, and flow rate measurements for particle analysers. Our calibration schedule, in full, is available here:
https://www.ukas.com/wp-content/uploads/schedule_uploads/00001/0478Calibration%20Multiple.pdf

However, due to the logistical requirements of supplying calibration and other test gases to the chemiluminescent NO_y instruments, we are forced to deviate from our accredited procedure. The tests which are carried out according to our procedures, and are, thus, accredited, are the calibration of ozone, carbon monoxide, and sulphur dioxide analysers, and the flow rate measurement of particle analysers.

We are not currently accredited for the on-site calibration of NO_y chemiluminescent analysers, CH_4/CO_2 analysers, the calibration of single channel NO_2 analysers, or for the non-flow aspects of the FIDAS calibrations. All results relating to these analyser types are not, therefore, ISO 17025 compliant.