

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

**Estimation of Measurement
Uncertainty in Network Data**

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March 2007

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Approved on behalf of Managing Director, NPL
By Dr Melanie Williams, Division of Quality of Life

EXECUTIVE SUMMARY

This NPL Report is an introduction to the measurement uncertainties associated with data produced by the Airborne Particulate Concentrations and Numbers Network.

The audit and calibration of the network instruments provides correction factors required to eliminate bias from the measurement results. These are applied during the data ratification process. The tests conducted during the audits, and during routine testing of the instruments, also allow an estimation of the random uncertainty in the measurement process. Further investigation may be required to reliably quantify the uncertainties in these data.

For each model of instrument on the Network the uncertainty associated with the measurement, *relative to other similar instruments*, has been estimated. Note that the term 'uncertainty' is usually applied in a broader sense, as described in the Introduction.

- The results produced by the CPCs are strongly dependent on the low size cut-off point, which varies between models, making it impossible to directly compare different models. There are two modes of detection (single particle and photometric) that are commonly used during Network operation, and therefore two uncertainty estimations. The greatest contributions to uncertainty are detector drift and calibration. Switching between detection modes also has some measurement issues.
- The automatic nitrate analyser is a more complicated instrument, which relies on a series of assumptions and conversion factors. It is calibrated several times a year, but detector drift between calibrations is a large contribution to the overall uncertainty, as are converter and collection efficiencies.
- When functioning correctly, the main problem with the automatic carbon instruments is that the measurand is different to manual (reference) methods for OC/EC. However, the estimation of uncertainty given in this report is for a fully functioning instrument, compared to another of the same type.
- Daily nitrate, sulphate and chloride filters are analysed manually in a laboratory and the uncertainty in the analytical results is low due to strict QA/QC procedures. However, due to the method of sample collection, particle-laden filters can be exposed to ambient temperatures and gases for up to two weeks. During this time, it is possible that some volatile species are removed from the filter, and that some species are involved in chemical reactions with ambient gases, so that sampling and storage uncertainties can be significant.
- SMPS uncertainties have not been estimated because the instruments are currently being replaced with a different model. Their uncertainty will be addressed at a later date.

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INTRODUCTION

This NPL Report is an introduction to the measurement uncertainties associated with data produced by the Airborne Particulate Concentrations and Numbers Network.

Until we have robust methods for calibrating and otherwise testing the instruments used in the Network, any attempt to reliably quantify the uncertainties is likely to be approximate. The following text serves only to highlight some of the issues that have been uncovered through site audits and other experience with these analysers. Further investigation will be required to reliably quantify the uncertainties in these data.

Before discussing the uncertainty of a measurement, it is important to clarify the quantity being measured. The amount of ozone in a sample of air can be expressed as an amount fraction in mol/mol or as a mass concentration in $\mu\text{g}\cdot\text{m}^{-3}$. This does not need clarification. The amount of PM_{10} , on the other hand, depends significantly on the method of collecting and weighing the sample, and is effectively defined as, 'the result of a measurement made by the reference method, published as...' (a method-defined measurand).

This has important practical consequences because there is a clear distinction between the uncertainty of the method and absolute uncertainty. The uncertainty of the method can be used to compare results from similar measurements, or the same system over time (method reproducibility and repeatability). The uncertainty of the result in absolute terms (with respect to the SI units used) is appropriate when results from different methods are being compared.

The audit and calibration of the network instruments¹ provides correction factors required to eliminate bias from the measurement results. These are applied during the data ratification process. The tests conducted during the audits, and during routine testing of the instruments, also allow an estimation of the random uncertainty in the measurement process. The uncertainty estimations provided in this report reflect the relative uncertainty of ratified data from a fully functioning instrument. It does not take into account data produced when any part of the instrument is malfunctioning. All uncertainties in this report are quoted as expanded ($k=2$) uncertainties, corresponding to a confidence interval of about 95%.

1 CONDENSATION PARTICLE COUNTERS

Measurand

A CPC counts the number of individual particles in a sampled volume of air. The smallest particle that can be detected is governed by the degree of supersaturation of the butanol vapour. This is different for every type and model of CPC, so two different models run in parallel would give different results. For this reason, in this report only the uncertainty for the TSI 3022A CPC is discussed. This model has a low size cut-off at around 7nm (50% efficiency). By 20nm, close to 100% of particles are detected.

Very large particles (tens of microns in diameter) are lost by impaction on the inside of the CPC. This can also vary between models but has little effect because of the low numbers of very large particles in ambient air.

Theory of Operation

Ambient air is drawn into the CPC at a 'high' flow rate of 1.5 l/min, to minimise diffusional losses between the inlet and the sensor. The flow reaching the sensor, however, is a nominal 0.3 l/min. Inside the CPC a pool of butanol is heated and the supersaturated vapour condenses onto the particles in the airflow, so that they are large enough to be detected optically. An average measurement result is produced every 15 minutes.

There are three modes of detection:

1. Single particle 'real time' detection is used when there are less than 1000 p/cm³ (particles per cubic centimetre). The saturated particles interact with a laser beam, where the light scattered by each individual droplet is collected by a photodetector and generates an electrical pulse, which is counted automatically. This situation is rarely reached at network locations, where particle concentrations tend to be between 4000 and 300,000 p/cm³.
2. Single particle 'live time' counting is used when counts are between 1000 and 10,000 p/cm³. This is common at most network sites, although Marylebone Road rarely dips below 10,000 p/cm³. In this mode the CPC performs an automatic deadtime correction to allow for particles expected to be missed by the optical detector.
3. Photometric detection is used for particle concentrations greater than 10,000 p/cm³. The detector no longer attempts to count individual particles, instead it produces a DC voltage proportional to the light scattered from all of the particles in the sample. The manufacturer calibrates the voltage from the detector against a known concentration of particles during the annual service.

Detector Calibration (photometric mode only)

During calibration at TSI, an electrostatic mobility classifier and a dilutor are used to generate 20 concentrations of monodisperse, monocharged 50nm NaCl aerosol in the range 10,000 to 500,000 p/cm³ (uncertainty is assumed to be +/- 3%). These are measured by the CPC and the deviation between the independent value from a TSI 3068 electrometer and the

detector response is calculated. This factor is used during ratification to scale the data and eliminate bias.

To scale data from the instruments, the instrument drift is assessed by comparison of the post service calibration and as-found calibration of the same instrument one year later. Any difference in sensitivity is assumed to have occurred linearly, and a monthly correction factor (F) is applied to the data to reflect this. Examples of the annual drift for several instruments are given in Table 1.

CPC	Post Service 05/06	Before Service 06/07	Post Service 06/07
Birmingham	3%	-38%	5%
Port Talbot	1%	-9%	-2%
Marylebone Road	-1%	5%	-6%
Manchester	-4%	-57%	1%
Glasgow	-2%	-14%	-1%

Table 1 Average % deviation of the instrument response from the electrometer based concentration, for at least 5 calibration points in the normal working range of the instrument.

Measurement Equation

The overall measurement equation is simple:

$$C_p = \frac{N_{tot}}{V_{air}} * F \tag{1}$$

C_p is the concentration of particles (m^{-3})

N_{tot} is the total number of sampled particles, corrected by annual calibration

V_{air} is the volume of ambient air sampled (m^3)

F is a correction factor for drift

Uncertainty Estimation

The uncertainty in the measurement result can be described by the following equation:

$$\frac{u(C_p)}{C_p} = \sqrt{\left[\frac{u(N_{tot})}{N_{tot}}\right]^2 + \left[\frac{u(V_{air})}{V_{air}}\right]^2 + \left[\frac{u(F)}{F}\right]^2} \tag{2}$$

- Uncertainty in N_{tot} at lower concentrations is strongly dependent on the accuracy of the deadtime correction. Leaks and particles adhering to the inside of the CPC can introduce some uncertainty, but this is minimised by regular leak checks and operating at high flow. There is no background subtraction when the CPC is operated in single counting mode.

TSI estimate that the background count is only 0.01 p/cm^3 . During the audit, NPL measured the zero response of the analysers with a HEPA filter and the average analyser response was 1.1 p/cm^3 , which is negligible and therefore does not need to be included in the uncertainty estimation.

- Uncertainty in total number of particles at high concentrations is characterised during the annual calibration by the manufacturer and a correction factor is applied to the data during ratification to minimise bias (described above). It is assumed that in photometric mode leaks, losses and background counts are accounted for by the calibration.
- The uncertainty of analyser flow rate is taken to be $\pm 5\%$ ($k=2$) at the low flows used by the CPC, based on flow rate measurements made at the audits. Flow rate is multiplied by sampling time (it is assumed that the uncertainty in time is negligible) to calculate V_{air} .
- A drift correction is applied to the data to allow for a drifting detector response and drifting flow rate (measured during audits) over time. This greatly reduces the error in the measurement, but the uncertainty in the correction itself must contribute to the uncertainty budget.

Input variables (single counting):

	Distribution	$k=1$	$k=2$
Flow	Normal	2.5	
Detector response (deadtime correction)	Rectangular	$2 / \sqrt{3}$	
Correction Factor for drift over time	Rectangular	$5 / \sqrt{3}$	
Total		4.0%	8.0%

Input variables (photometric):

	Distribution	$k=1$	$k=2$
Flow	Normal	2.5	
Factor from detector calibration	Normal	3	
Correction factor for drift over time	Rectangular	$5 / \sqrt{3}$	
TSI aerosol concentration*	Normal	1.5	
Total		5.1%	10.2%

* The concentrations of the aerosols generated by TSI have an estimated expanded uncertainty of 3%, thus 1.5% unexpanded.

For the single counting mode, a reasonable estimation of uncertainty in the final measurement result is 8%. For the photometric mode, a reasonable estimation of uncertainty in the final measurement result is 10%. These estimations agree well with the manufacturer, who calculates that the accuracy of measurements below $500,000 \text{ p/cm}^3$ is 10% (the maximum particle concentration seen at Marylebone Road is about $300,000 \text{ p/cm}^3$).

Data from tests carried out at NPL using co-located samplers, have shown large differences between models. These tests have also shown anomalies that occur as the measurement mode

switches from particle counting to photometric modes. This problem appears to be further complicated by evidence of hysteresis effects around the switchover point (10,000 p/cm³), as shown in Figure 1:

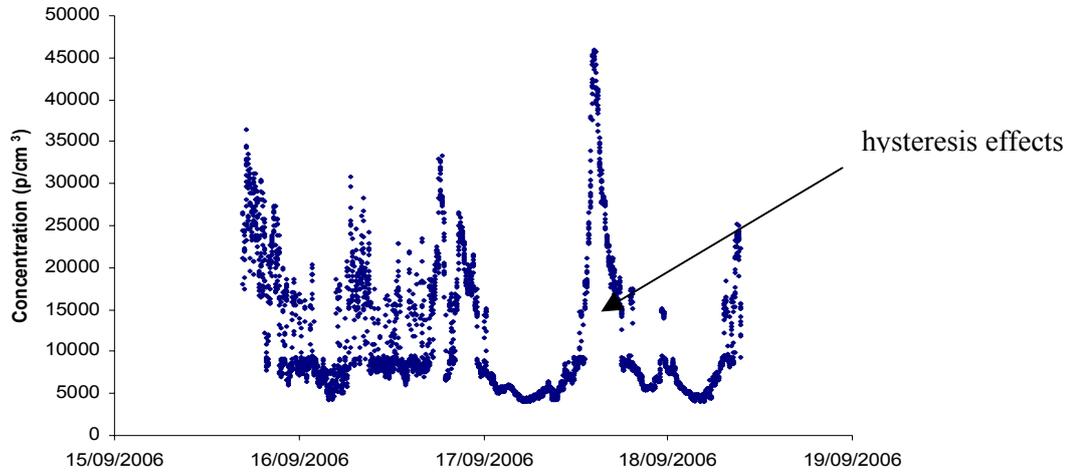


Figure 1 Scatter plot of ambient particle number around the switchover point between the single counting and photometric detection modes.

To some extent, this phenomenon can be corrected for using appropriate calibration factors. Regular maintenance also reduces it. Further research and investigation is being carried out to quantify the effect of the problem.

2 CONTINUOUS NITRATE ANALYSERS

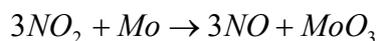
Measurand

The Thermo 8400N automatic nitrate analyser measures the concentration of nitrate (in particles smaller than $2.5\mu\text{m}$ in diameter) in a sampled volume of ambient air. Nitrate is commonly found as sodium nitrate and ammonium nitrate, generated through secondary atmospheric processes.

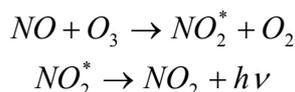
Theory of Operation

The nitrate analyser samples ambient air at a rate of 5 l/min, although only 1 l/min of this is analysed. Inside the instrument, the air enters a $\text{PM}_{2.5}$ cyclone to remove large particles and then an activated charcoal denuder to remove gaseous interferences. Particles in the air stream pass through a humidifier to maximise collection efficiency before they are forced through a critical orifice and impact onto a Nichrome flash strip. The manufacturer estimates that the collection efficiency is about 98%.

The duration of the sampling cycle is 10 minutes, followed by analysis of the collected nitrate and calculation of the ambient concentration. During analysis the flash strip is heated in a nitrogen atmosphere, releasing the nitrate in the sample as NO_x . Inside the NO_x chemiluminescence analyser, NO_2 is reduced to NO in a molybdenum converter:



The NO is exposed to an excess of ozone and each resulting NO_2 molecule emits a light photon:



A photomultiplier tube measures the emitted light, and the tube output voltage is proportional to the number of molecules present.

Before and after the analysis, the instrument is purged with nitrogen and a baseline reading is taken and subtracted from the sample response. The NO_x analyser is recalibrated every six months during routine service, and a span gas is analysed every 24 hours, using 5ppm NO/N_2 , which is certified at NPL and is traceable to primary standards.

The mass of nitrate collected during the sampling period is calculated by the instrument as a function of analyser flow, molecular weight of nitrate, molar concentration, concentration of NO_x , and time.

Aqueous Calibration

Aqueous solutions of KNO_3 are used to test instrument response. A known volume of the solution is measured by syringe and deposited onto the flash strip. (The zero is determined in this way also, by using deionised water). The instrument then analyses it as it would a normal sample, thus allowing the user to test more of the process than by span gas analysis alone. The instrument response to the known mass of nitrate is used during ratification to correct data.

The results of a typical calibration are shown in Figure 2:

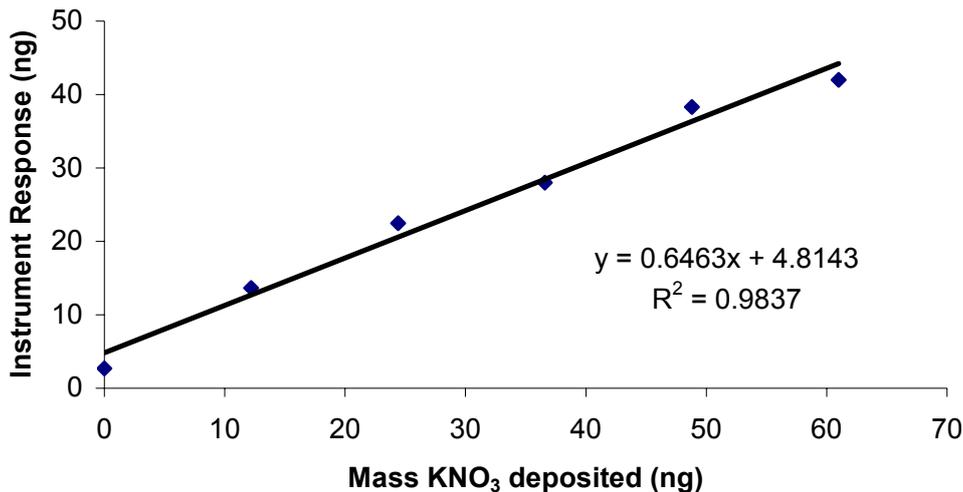


Figure 2 Response of Nitrate instrument to aqueous KNO_3 solution

The slope is used as a correction factor (F) to remove bias from the result. The uncertainty in the correction factor, $u(F)$, has the following contributions:

- Uncertainty in the application of the correction factor over time. Drift is assumed to be linear between monthly determinations of F .
- User error. This has been estimated by repeated measurements.
- Uncertainty in the KNO_3 solution is estimated to be $\pm 1\%$. Drift in concentration of these standards is assumed to be negligible due to storage procedures.
- Accuracy of the syringe ($\pm 1\%$).

The intercept is not used in the correction because within the uncertainty of the measurement, probable values for the intercept include zero. Uncertainty in the correction factor, including contributions listed above, is estimated to be 20% ($k=2$), where the major contributing factor is drift.

Measurement Equation

The overall measurement equation is:

$$C_{\text{NO}_3} = \frac{m_{\text{NO}_3}}{V_{\text{air}}} * F \quad (3)$$

C_{NO_3} is the concentration of nitrate in the ambient air (ng. m⁻³)

m_{NO_3} is the mass of nitrate determined by the instrument (ng)

V_{air} is the volume of ambient air sampled (m³)

F is a correction factor based on the aqueous calibration

The instrument calculates m_{NO_3} by subtracting the baseline from the measured concentration of NOx and then converting NOx concentration to nitrate mass. This conversion factor assumes that one molecule of NOx directly converts to one molecule of NO₃⁻ and is a function of the molar volume of an ideal gas, molecular mass of nitrate, and analyser flow rate, as shown ²:

$$m_{NO_3} = Q * \frac{M_r}{V_{molar}} \int C dt \quad (4)$$

Q is the analyser flow rate (0.015 l. s⁻¹)

M_r is the molecular mass of nitrate (62.0049 g. mol⁻¹)

V_{molar} is the molar volume of a gas at standard conditions (24.465 l)

C is the instantaneous mole fraction of NOx (ppb)

dt is the time resolution (s)

Uncertainty Estimation

The uncertainty of the measurement result can be estimated by the equation (5):

$$\frac{u(C_{NO_3})}{C_{NO_3}} = \sqrt{\left[\frac{u(m_{NO_3})}{m_{NO_3}} \right]^2 + \left[\frac{u(V_{air})}{V_{air}} \right]^2 + \left[\frac{u(F)}{F} \right]^2} \quad (5)$$

- Uncertainty in the flow rate (temperature and pressure sensors are used to correct the flow rate to standard conditions). The expanded uncertainty for measurements of flow at this flow rate is taken to be ± 3%. Flow rate is multiplied by time (assume uncertainty is negligible) to calculate V_{air} .
- Uncertainty in the mass of nitrate determined by the instrument has many contributions, including analyser flow rate, NOx concentration and baseline subtraction. We assume that the uncertainty in molar volume and molecular mass are negligible. The NOx concentration is believed to be the primary source of errors, which can be separated into three categories: collection, conversion and calibration.

Collection. The instrument assumes that particle collection efficiency is 100%, although it is expected that some particles are lost between the sampling head and the impaction strip. It also assumes that the denuder successfully removes any interferences. Evaporative losses² for volatile species like ammonium nitrate have been reported to be up to 6% of the total nitrate concentration. A study by Wittig et al.⁵ indicated that collection efficiency can be as low as 85%, but in a well-maintained instrument, the expanded uncertainty is estimated to be no more than 10%.

Conversion. Particles that are collected on the flash strip are subject to analysis inside a closed cell. It has been previously noted in other studies that the drift of the cell vacuum can significantly affect the final result and the analyser flow, used in equation (4), also has an associated uncertainty. The manufacturer suggests that the molybdenum converter efficiencies should be in the region of 95 to 100% at NO₂ amount fractions less than 0.5 ppm. However, site audits have indicated a problem with the NO_x analyser appearing to have a different response to NO than NO₂, consistent with poor converter efficiency. Measurements carried out on the nitrate analysers have shown conversion efficiencies of approximately 50% for NO₂ amount fractions greater than 5 ppm. Replacement molybdenum converters have been ordered. The uncertainty estimation below is for a fully functioning instrument.

Calibration. The NO_x analyser is calibrated only during service, however, the bias due to the automatic calibration and detector drift is removed by the correction factor, F .

- Allowing 10% uncertainty for conversion efficiency and 10% for collection efficiency (both $k=2$), $u(m_{NO3})$ is 14.1%.
- Uncertainty in F is discussed in the previous section of this report. $u(F)$ is estimated to be 10%.
- Losses and leaks of particles and gases within the instrument. It is difficult to quantify these losses but regular leak testing, inlet cleaning and routine maintenance reduce them.

Input variables:

	Distribution	$k=1$	$k=2$
Flow	Normal	1.5	
Nitrate mass determined by instrument	Rectangular	$7.1 / \sqrt{3}$	
Aqueous calibration correction factor	Rectangular	$10 / \sqrt{3}$	
Total		7.2%	14.4%

The US EPA³ recently calculated that the average relative standard deviation for 8400N Nitrate analysers was 5.2%; our estimate is therefore somewhat larger. The EPA study provides a full discussion of the differences between this automatic instrument and the reference method (as described here in Section 4). Harrison et al.⁴ and Wittig et al.⁵ have carried out more detailed investigations into the operational uncertainty contributions for this instrument.

3 AMBIENT CARBON ANALYSERS

Measurand

The carbon content of particles can be classified into two types, elemental and organic. Elemental carbon (also known as black carbon) is emitted during combustion processes. Sources of organic carbon include traffic, industrial combustion and the degradation of carbon-containing materials.

This measurement method relies on the different oxidation characteristics of the two types of carbon to distinguish between them. Carbon which oxidises at $<350^{\circ}\text{C}$ is assumed to be organic, carbon that oxidises between 350°C and 750°C is termed 'elemental'. However, it is generally agreed that there is some overlap between the two categories, that the relevant temperature varies depending on other gases that are present during analysis, and that some carbon can be converted between the categories during the analysis. Therefore, each analysis method is likely to yield a different result.

The Thermo 5400 Automatic Carbon analyser measures carbon within particles between $10\mu\text{m}$ and 100nm .

Theory of Operation

The 5400 carbon instrument samples ambient air at 16.7 l/min through a PM_{10} size selective inlet. During the collection cycle (either 3 hours or 1 hour) particulates accumulate on a collector by impaction. During the analysis stage, this collector is heated to oxidise the carbon, while sampling continues in a second collector.

The particulates are heated in ambient air to 350°C to oxidise the organic carbon, then the temperature is ramped up to 750°C to convert the elemental carbon to CO_2 . The instrument uses zero air to take a baseline measurement that is later subtracted. It outputs values for organic carbon and total carbon. Elemental carbon can be calculated by the user as the difference between these two values.

Calibration

The LiCor CO_2 sensor generates an output voltage, which can be related to the volume of CO_2 by the following equation:

$$\text{CO}_2 \text{ volume } (\mu\text{l}) = ax^2 + bx + c$$

Where x is the voltage output as a percentage of the full voltage scale. The detector response is calibrated with two span gases (nominally 0.25% and $0.45\% \text{CO}_2/\text{N}_2$) that are measured every 72 hours. The span gases are certified at NPL and are traceable to primary standards and are known to $\pm 0.25\%$. The instrument applies corrections for temperature and pressure at various stages in the calculation.

It is necessary to apply a correction factor during ratification, based on the instrument response to a known concentration of CO_2 .

Measurement Equation

The overall measurement equation for total carbon is:

$$C_{TC} = \frac{(V_{CO_2} - V_{CO_2,0}) * c}{V_{air}} * F \quad (6)$$

C_{TC} is the concentration of total carbon in the ambient air ($\mu\text{g} \cdot \text{m}^{-3}$)

V_{CO_2} is the volume of CO_2 in the analysis loop resulting from the sample oxidation (μl)

$V_{CO_2,0}$ is the volume of CO_2 in the analysis loop when purged with zero air (μl)

V_{air} the volume of ambient air entering the instrument, corrected to standard conditions (m^3)

F is a correction factor

c is a constant which describes the relationship between CO_2 volume and mass of carbon, $0.493 \mu\text{g} \cdot \mu\text{l}^{-1}$. It is derived from the universal gas equation and the atomic mass of C as a proportion of CO_2 .

Uncertainty Estimation

The uncertainty can be estimated with the following equation:

$$\frac{u(C_{TC})}{C_{TC}} = \sqrt{\left[\frac{\sqrt{u(V_{CO_2})^2 + u(V_{CO_2,0})^2}}{V_{CO_2} - V_{CO_2,0}} \right]^2 + \left[\frac{u(V_{air})}{V_{air}} \right]^2 + \left[\frac{u(c)}{c} \right]^2 + \left[\frac{u(F)}{F} \right]^2} \quad (7)$$

There are many contributions to the uncertainty of this instrument:

- Uncertainty in the volume of ambient air sampled (including uncertainties in the mass flow controller, temperature and pressure correction). This has been reduced and estimated with a flow calibration during the routine audit round. Data is corrected during ratification. Measurements of analyser flows have expanded uncertainties of $\pm 3\%$.
- Uncertainty in CO_2 volume measured by the detector. The data ratification process applies a correction (F) for detector response so this uncertainty contribution only includes uncertainty in cell pressure, collection efficiency (10%), oxidation efficiency (10%) and repeatability. Repeatability errors were measured at the site audits, with standard deviations of repeat measurements being 0.2% of value.
- Uncertainty in the correction factor, which is based on the instrument response to a span gas of known concentration. This includes uncertainty in the concentration of the span gases, and application of the drift correction over time.
- Uncertainty in the constant, c , although this is derived from SI units and the uncertainty is assumed to be negligible.

- Losses and leaks of particles and CO₂ gas within the instrument. It is difficult to quantify these losses but they are reduced by regular leak testing, inlet cleaning and routine maintenance.

Input variables:

	Distribution	<i>k</i> =1	<i>k</i> =2
Flow	Normal	1.5	
ΔV (detector response)	Rectangular	$7.1 / \sqrt{3}$	
Correction Factor	Rectangular	$3 / \sqrt{3}$	
Total		4.7%	9.4%

The analyser manual states quite clearly that the choice of burn temperatures, selectable in software, is likely to have significant effect on the range of organic species measured at each stage of the analysis cycle. Thus, the overall uncertainties in organic carbon and elemental carbon data are entirely dependent upon user-selectable parameters. Any comparison with data obtained using alternative methods is highly likely to show significant differences in concentrations of EC and OC species. Also, the fact that particles smaller than 100nm are not collected is expected to make a significant difference compared with methods that collect particles on a filter.

4 DAILY NITRATE, SULPHATE AND CHLORIDE

Measurand

This method measures the concentration of non-volatile, chemically stable, water-soluble nitrate, sulphate and chloride ions in the PM₁₀ fraction of airborne particulates. It does *not* measure the concentrations of specific compounds such as ammonium nitrate or sodium nitrate.

Due to the method of sample collection, particle-laden filters can be exposed to ambient temperatures and gases for up to two weeks. During this time, it is possible that some volatile species (such as ammonium nitrate) are removed from the filter, particularly during the summer months. It is also possible that some species are involved in chemical reactions with ambient gases, during or after sampling.

For these reasons, and the different sampling method, the concentrations of nitrate measured by the automatic nitrate instruments can be different from the results of the daily nitrate filters.

Theory of Operation

Partisol 2025 samplers draw a known volume of air through PTFE coated glass fibre (Emfab) filters over a 24-hour period, at a rate of nominally 16.7 l/min. The samplers are fitted with PM₁₀ inlets. Nitrate, sulphate and chloride species contained within the particulates on the sampled filters are extracted by sonication in a known mass of deionised water. The extracted solution is analysed by ion chromatography (IC).

In the IC the sample enters an anion exchange column that separates the anions. The chloride ion is detected first, followed by the larger nitrate and then sulphate ions (see Figure 3). The detector is a conductivity cell.

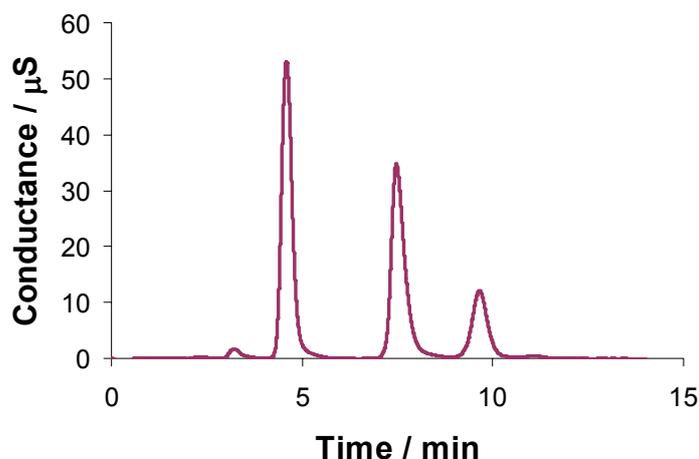


Figure 3 Example of a typical ion chromatograph

Calibration

Calibration standards are prepared from standard solutions of chloride, nitrate and sulphate. The ranges of concentrations for each anion bracket the expected concentrations of the samples from the Network, and are given in Table 2.

Anion	Min ($\mu\text{g. ml}^{-1}$)	Max ($\mu\text{g. ml}^{-1}$)
Chloride	0.05	30
Nitrate	0.16	100
Sulphate	0.24	150

Table 2 Calibration standard concentration ranges

At least three calibration standards are measured during every analysis, and they are used to relate the sample peak area to concentration of the ion in the extracted solution.

Then:

$$m_{i,f} = c_{i,sol} * V_{sol} \quad (8)$$

$m_{i,f}$ is the mass of the ion on the exposed filter (μg)

$c_{i,sol}$ is the concentration of the ion in the extracted solution ($\mu\text{g. ml}^{-1}$)

V_{sol} is the volume of the extracted solution (ml)

Measurement Equation

The overall measurement equation is:

$$C_I = \frac{\Delta m}{Ft} * D \quad (9)$$

C_I is the concentration of the ion in ambient air ($\mu\text{g. m}^{-3}$)

Δm is the mass difference of the ion on the exposed filter and blank filter (μg)

F is the sampler flow rate ($\text{m}^3. \text{h}^{-1}$)

t is the total sampling time (h)

D is a factor applied to correct for drift

Uncertainty Estimation

The uncertainty in the final calculated concentration can be described as:

$$\frac{u(C_I)}{C_I} = \sqrt{\left[\frac{u(\Delta m)}{\Delta m}\right]^2 + \left[\frac{u(D)}{D}\right]^2 + \left[\frac{u(F)}{F}\right]^2 + \left[\frac{u(t)}{t}\right]^2} \quad (10)$$

- The extraction efficiency of the sonication process is assumed to be $100\% \pm 10\%$ ($k=2$) for each of the anions. This has been determined at NPL by repeated extractions of the same filter.
- The preparation of the calibration standards is done volumetrically, and they are periodically checked against a set of gravimetrically prepared standards from NPL. Additionally, two intercomparison exercises have been carried out since June 2005, showing excellent agreement between three laboratories⁶. It is estimated that the uncertainty in the preparation of the calibration standards is 2.4% ($k=2$) including contributions from the volumetric preparation and the purchased anion stock solution.
- The measurement of both samples and calibration standards relies on accurate analysis by the ion chromatograph, particularly well-resolved peaks and accurate integration. Extensive method development has ensured the former, but integration can introduce errors, especially at low concentrations. To reduce this problem, repeat measurements are made of every sample. Uncertainty from the analysis is presumed to be less than 2% ($k=2$), for an 'average' sample.
- Blank filters are analysed with every analysis run. It is very rare that the method is able to detect any nitrate or sulphate on a blank filter, although chloride is present in low amounts, and this is subtracted. The variation of ion masses present on the blank filters introduces another small element of uncertainty, estimated to be 0.5% ($k=2$).
- Calibration curves are generated by NPL's XGenline programme⁷. The uncertainty in the generation of this line and the unknown values from the equation of the line is less than 0.5% ($k=2$).
- Although time can be measured very accurately, Partisol flow tends to fluctuate. Flows are measured accurately during the audit round and a correction factor is applied to the data. However, between the annual audit the flow rates can change by up to 1.07 l/min, as shown in Table 3. The flow is assumed to drift linearly throughout the year and an appropriate correction factor is applied to the data between the audits. The uncertainty assigned to this measurement of flow is 3%. Uncertainty in the assumption of drift is estimated at 10%.
- Uncertainties due to sampling and storage are not included.

Flow rate (l/min) recorded by BIOS during audit (set point 16.7 l/min)

	Harwell	Belfast	Marylebone	N Kensington
2005	15.40	15.76	16.67	16.93
2006	16.47	16.39	16.09	16.51

Table 3 Partisol flow rates at the annual audits 2005-2006

Input variables:

	Distribution	<i>k</i> =1	<i>k</i> =2
Flow	Normal	1.5	
Δm	Rectangular	$5.3 / \sqrt{3}$	
Correction Factor for drift	Rectangular	$5 / \sqrt{3}$	
Total		4.5%	9.0%

The 5.3% uncertainty for Δm has been estimated by adding in quadrature the associated uncertainty contributions.

5 SCANNING MOBILITY PARTICLE SIZER

At the time of writing this report, the three SMPS instruments were being decommissioned, and a new model from TSI Instruments will replace them. It is recommended that an uncertainty estimation for the SMPS be undertaken after one year of operation, when audit and calibration data is available.

6 INSTRUMENT DETAILS

<u>Manufacturer</u>	<u>Instrument</u>	<u>Model</u>
TSI Instruments Ltd. Lancaster Road Cressex Business Park High Wycombe Buckinghamshire HP12 3QP UK	CPC	3022A
Thermo Fisher Scientific, Inc. 81 Wyman Street Waltham MA 02454 USA	SMPS	3936 L75
	Automatic Nitrate	8400N
	Automatic Carbon	5400
	Partisol	2025

NPL would like to extend thanks to Nick Cussens at TSI Instruments Ltd, and to Mel Hadfield at Air Monitors Ltd, for providing clarification of the measurement and calibration processes of the field instruments.

7 SUMMARY TABLE

	Major Contributions	Expanded Uncertainty
CPC 3022A	Deadtime correction	8% (single counting)
	Detector drift	10.2% (photometric mode)
	TSI monodisperse aerosol concentrations	
	TSI calibration factor	
	Ambient air flow rate	
	Hysteresis effects	
Nitrate 8400N	Detector drift	14.4%
	KNO ₃ (aq) concentration	
	Syringe calibration	
	Ambient air flow rate	
	Analyser flow rate	
	Baseline subtraction	
	Particle collection efficiency	
	Denuder efficiency	
	Conversion efficiency	
	Analyser calibration	
Carbon 5400	Ambient air flow rate	9.4%
	Calibration gas concentration	
	Detector drift	
	Collection efficiency	
	Oxidation efficiency	
Partisol/IC	Ambient air flow rate	9.0%
	Extraction efficiency	
	Calibration standard concentration	
	IC peak integration	
	Blank subtraction	

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