

NPL REPORT
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**Particle Measurement
Programme –**

Analysis of Errors

DRAFT REPORT

**Richard Gilham and
Paul Quincey**

RESTRICTED

July 2007

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By xxx, Business Leader, Division of Quality of Life

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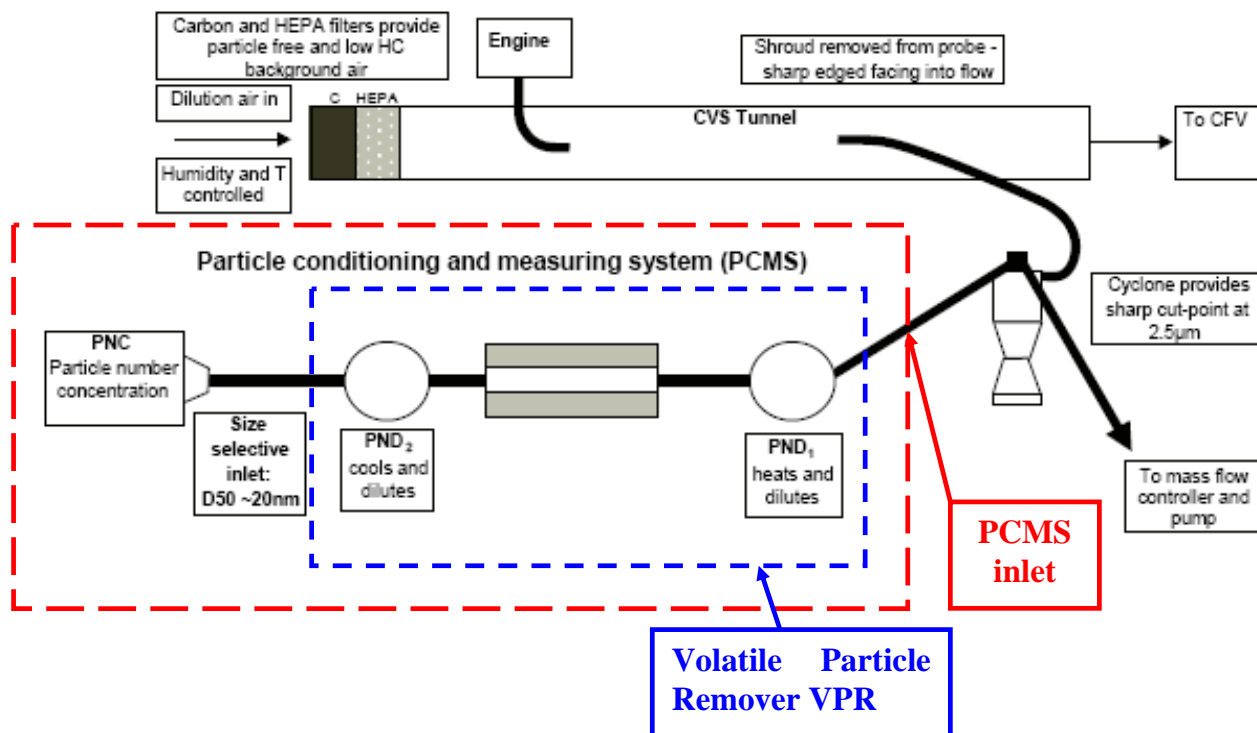


Figure 1: Schematic diagram of the measurement system

1 Clarification of the measurements

The aim of this document is to evaluate uncertainties (errors) in specific vehicle emission particle measurements, linking them to the calibrations and checks that are required or that may be needed in the measurement procedures. Before analysing the uncertainties of a measurement, it is important to clarify what we are trying to measure.

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The system under consideration is limited to the Particle Conditioning and Measuring System (PCMS), outlined in the dashed box in Figure 1 above. Aspects of the measurement upstream of the inlet to the PCMS, including the cyclone that removes larger particles, are not considered here.

The PCMS, for present purposes, is a system for determining the number concentration of non-volatile particles within a certain size range at the PCMS inlet. “Non-volatile” particles are defined operationally below. In practice the PCMS dilutes the air stream before the number concentration is measured at the Particle Number Counter (PNC), to bring concentrations below $10,000 \text{ cm}^{-3}$ at the PNC, and to reduce new particle nucleation. The measured number concentration at the PNC therefore

needs to be combined with a measured dilution factor to produce the inlet concentration. The elements that dilute the sample and remove the volatile particles are together labelled the Volatile Particle Remover (VPR).

The analysis below will generally assume that the airstream to be measured contains typical post-Diesel Particulate Filter (DPF) particle distributions.

Three separate measurements are considered here:

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1.1 Particle number concentration

This is the most important measured quantity, which will ultimately determine whether an engine passes or fails an emissions test for particle numbers. The final result incorporates the total volume of diluted exhaust gas and the distance covered by the test to give a value of emitted particles per kilometre travelled, but the measured quantity here is:

Number concentration (in cm^{-3}) of non-volatile particles in the nominal size range 23 nm – 2.5 μm at the PCMS inlet. The air volume is to be corrected to Standard Temperature and Pressure (273.2K and 101.33 kPa).

Typical number concentrations for a post-DPF vehicle during a test range from close to zero to 500,000 cm^{-3} . In practice concentrations below 5,000 cm^{-3} will contribute little to the final result, so this report will focus on the range 5,000 to 500,000 cm^{-3} .

It is important to note that the definitions of volatility, size range and indeed number concentration are in practice defined operationally. The role of the uncertainty analysis is to evaluate possible variations of the measurement result when implementing the procedures, and not to evaluate uncertainties with respect to absolute (SI) definitions.

The inlet concentrations are diluted within the VPR, in part to keep concentrations within the range in which standard PNCs count individual particles without excessive coincidence errors, deemed to be < 10,000 cm^{-3} .

The UNECE proposed procedure [1] allows total dilutions between 100 and 7,500 (10 to 500 on PNDF₁ combined with 10 to 15 on PNDF₂). With the very high dilution factors, the concentrations to be measured downstream in the VPR tests below become very small – of the order 1 cm^{-3} and 1 ppm. This would make accurate measurement very difficult. This report considers only dilution factors of around 150, so that the concentration range to be measured by the PNC for this measurement is around 30 to 3,000 cm^{-3} .

The low size cut-off curve for the PNC is defined by the UNECE proposed procedure [1] as an inlet efficiency of 50±12% at 23 nm and > 90% at 41 nm. However, there are no specifications for how this performance is to be checked. The high size limit at 2.5 μm in practice has very little effect on the number count, as the numbers of large particles are relatively small, and the high size limit will not be considered further.

The approach set out in the proposed UNECE procedure [1] implies that the basic measurement equation to be used is:

$$C_{\text{inlet}} = C_{\text{PNC}} \times F_{\text{gas dilution}} \quad (1)$$

Where F is the gas dilution factor through the PCMS at the time of the measurement.

This has the advantage of simplicity, as considerations of size distribution are not needed. However, it makes no allowance for particle penetration efficiency (Section 1.2), which could theoretically introduce errors of up to 40%, if all the particles are around 30 nm in size and the penetration efficiency is the allowed minimum of 60% [2].

As the penetration efficiency needs to be determined in a separate measurement, it is possible to correct for it after using Equation 1, though this is not explicit in the procedure. If this is done, the gas dilution factor cancels out. It is therefore simplest to ignore the gas dilution factor altogether and instead use Equation 2:

$$C_{\text{inlet}} = C_{\text{PNC}} \times F_{\text{particle dilution}} \quad (2)$$

Where F is the particle dilution factor through the PCMS at the time of the measurement.

However, F will be measured (and different) for the three different particle sizes that are measured, so that a better equation is:

$$C_{\text{inlet}} = C_{\text{PNC}} \times F(\text{av})_{\text{particle dilution}} \quad (3)$$

where F(av) is a weighted average of the three particle dilution factors reflecting the typical particle size distribution involved.

In both cases care must be taken that the method used to determine the dilution factor of the PCMS does not itself change the performance of the PCMS from how it is during a vehicle measurement, for example by changing relevant flows.

The effect of choosing between these two approaches is discussed in Annex 4.

1.2 Particle penetration efficiency

Alongside the potential for correcting the number concentration data, there is a separate requirement to measure particle penetration efficiencies to show that they are above certain values, as high particle losses might unacceptably affect the validity of the measurements.

The quantity to be measured is:

The probability of a non-volatile particle of a specified size, after entering the VPR inlet, being measured by the PNC instrument.

The loss-free dilution factor is assumed to be found by measuring the dilution of a stable, non-reactive gas mixture (typically NO). The basic measurement equation is:

$$E(d)_{\text{particle penetration}} = F_{\text{gas dilution}} / F(d)_{\text{particle dilution}} \quad (4)$$

Where $E(d)$ and $F(d)$ show that the penetration efficiencies apply to particles of specific sizes, in this case 30nm, 50 nm and 100nm.

Of course the VPR heating and dilution settings must be the same for both the gas and particle measurements.

The particle penetration will vary to some extent with the heating and dilution settings chosen, and with the particle concentration.

The Draft Volatile Particle Remover Calibration Procedure [2] requires the concentration of the test particles to be between 5,000 and 10,000 cm^{-3} , and recommends the concentration of the test gas (eg NO) is $> 5,000$ ppm. With a dilution factor of 150, the downstream concentrations are therefore 33 to 66 cm^{-3} , and > 33 ppm respectively.

1.3 Volatile particle removal efficiency

There is a separate requirement that the VPR be demonstrated to remove a high proportion of volatile particles. In effect this defines what is meant by “non-volatile”.

The quantity being measured is:

The probability of a volatile particle of a specified type, after entering the VPR inlet, being removed before measurement by the PNC instrument.

The volatile particles are specified to be tetracontane (C_{40}) particles of around 30 nm diameter.

This measurement differs from the two previous ones in that an accurate evaluation is only required if the probability is close to the required minimum (99%). If, as is generally the case, the probability is significantly higher than this, the measurement is more of a validation check.

Two Methods are described in the VPR Calibration Procedure [2].

The basic measurement equation for Method 1 is:

$$E_{\text{volatile removal}} = 1 - (F_{\text{gas dilution}} / F(30\text{nm})_{\text{volatile particle "dilution"}}) \quad (5)$$

Arguably Equation 6 is more logical, but the difference is not expected to be critical.

$$E_{\text{volatile removal}} = 1 - (F(30\text{nm})_{\text{particle dilution}} / F(30\text{nm})_{\text{volatile particle "dilution"}}) \quad (6)$$

The VPR calibration procedure [2] specifies a volatile particle concentration of $>10,000 \text{ cm}^{-3}$. With a dilution factor of 150 and a removal efficiency of 99%, the downstream concentration will be $> 0.7 \text{ cm}^{-3}$ – a low value to measure accurately. However, as already mentioned, the removal efficiency just needs to be demonstrably better than 99%, rather than evaluated accurately.

The basic measurement equation for Method 2 is:

$$E_{\text{volatile removal}} = 1 - (C_{\text{PNC}} \cdot F_{\text{gas dilution (heater on)}} / C_{\text{PNC}} \cdot F_{\text{gas dilution (heater off)}}) \quad (7)$$

Where the “heater” refers to the part of the VPR designed to remove volatile particles, assumed to be capable of being switched off independently, when the specified volatile particles are being measured.

In this case the particle concentrations to be compared are $> 67 \text{ cm}^{-3}$ and $\sim 0.7 \text{ cm}^{-3}$. These values can be increased by having an input concentration much higher than $10,000 \text{ cm}^{-3}$ (which does not need to be measured).

2 Factors affecting the measurements

The tables below are meant to help focus on the factors that affect the various measurements set out in Section 1. They are not an exhaustive list, but should include the most important factors in each case.

2.1 Particle number concentration

$$C_{\text{inlet}} = C_{\text{PNC}} \times F_{\text{gas dilution}} \quad (1)$$

2.1.1 Factors affecting C_{PNC}

Factor	Symbol
PNC number concentration calibration accuracy <ul style="list-style-type: none"> - the accuracy is relative to other PNCs used for the same purpose - the calibration is done at a particle size well above the low size cut off (typically 50 – 100 nm) - the accuracy will vary with the number concentration due to factors such as coincidence (at concentrations above $\sim 5,000 \text{ cm}^{-3}$) and background noise (at low concentrations). 	C_1
PNC number concentration drift since calibration, eg due to change in flow rate.	C_2
Presence of volatile particles	C_3
Corrections to STP	C_4

2.1.2 Factors affecting $F_{\text{gas dilution}}$

Factor	Symbol
Accuracy of undiluted gas mixture concentration	G_1
Accuracy of the low concentration gas measurement (including calibration, drift, noise, non-linearity etc)	G_2
Presence of the test gas in the dilution air	G_3
Variations to the dilution system between the gas dilution determination and the particle concentration measurement (due to diluter set-up, drift, leaks, variable losses etc)	G_4

The value for $F_{\text{gas dilution}}$ is taken to be around 150, so that the concentration after the VPR is 33 ppm if a 5000 ppm NO mixture is used. The same factors affecting the measurements are assumed to apply to both the room temperature (needed for Method 2 of the volatile particle removal efficiency measurement) and the high temperature measurements of gas dilution factor.

2.1.3 Factors affecting the final result

Factor	Symbol
Comparability of the low size cut-offs of PNCs used for this purpose	F_1
Effect of particle penetration efficiency	F_2

Both of these factors will depend on the actual size distribution of the particles being emitted from the vehicle.

2.2 Particle penetration efficiency

$$E(d)_{\text{particle penetration}} = F_{\text{gas dilution}} / F(d)_{\text{particle dilution}} \quad (4)$$

The measurement consists of the determination of the dilution factor of the VPR for a gas mixture (as determined above), and the comparison of this with the dilution factor for non-volatile particles of a certain size and concentration range.

2.2.1 Factors affecting $F_{\text{particle dilution}}$

The determination of $F_{\text{particle dilution}}$ is assumed to follow the procedures set out in the draft VPR Calibration Procedure [2]. These contain two distinct possibilities, using one PNC instrument at the inlet and outlet, sequentially, or using two PNC instruments, at the inlet and outlet, simultaneously. These will be called “single PNC” and “dual PNC” respectively.

The PNC included in the system will generally not be suitable for particles close to 30 nm in size, so that one or two extra PNC instruments will be needed.

The (non-volatile) particle dilution factor at specific sizes is determined by generating synthetic particles of, for example, sodium chloride, with a narrow size range and an inlet concentration in the range 5,000 to 10,000 cm⁻³. The required sizes are 30 nm, 50 nm and 100 nm.

The value for $F_{\text{particle dilution}}$ is taken here to be 150, so that a typical concentration after the VPR is 33 to 66 cm⁻³.

2.2.1.1 Single PNC

Factor	Symbol
Nonlinearity affecting the ratio between the high concentration and the low concentration measurements	P_{S1}
Alterations to the system flows when the PNC is relocated	P_{S2}
Variations to the inlet concentration between “inlet” and “outlet” measurements (ie source drift)	P_{S3}
Variations in the performance of the diluter between “inlet” and “outlet” measurements (ie diluter drift)	P_{S4}

Presence of particles in the dilution air	P _{S5}
Background particle “noise”, ie release of particles from internal walls	P _{S6}
Variations to the particle dilution factor between its determination and the gas dilution factor measurement (due to diluter set-up, drift, variable losses etc)	P _{S7}
Corrections to STP (relative to gas measurement)	P _{S8}

2.2.1.2 Dual PNC

Factor	Symbol
Accuracy of the ratio of the “high PNC” and “low PNC” measurements, for example due to differences in calibration or flow rate or sampling lines between the two.	P _{D1}
Presence of particles in the dilution air	P _{D2}
Background particle “noise”, ie release of particles from internal walls	P _{D3}
Variations to the particle dilution factor between its determination and the gas dilution factor measurement (due to diluter set-up, drift, variable losses etc)	P _{D4}
Corrections to STP (relative to gas measurement)	P _{D5}

2.2.2 Factors affecting $F_{\text{gas dilution}}$

These are the same as in 2.1.2 above, with the exception of variations to the dilution factor, G_4 , which is covered by P_{S7} or P_{D4}.

2.3 Volatile particle removal efficiency

2.3.1 Method 1

$$E_{\text{volatile removal}} = 1 - (F_{\text{gas dilution}} / F_{(30\text{nm})\text{volatile particle "dilution"}}) \quad (5)$$

The measurement consists of the determination of the “dilution” factor (actually a combination of dilution and removal) of the VPR for air containing specially generated tetracontane (C₄₀) particles of around 30 nm diameter, and the comparison of this with the gas dilution factor (as determined above).

The volatile measurement is done by similar methods to the ordinary particle dilution measurement, but the dilution factor should be higher by a factor of at least 100. If the inlet concentration is 10,000 cm⁻³, the outlet concentration is expected to be less than 1 cm⁻³.

It will be assumed that the single PNC route will be followed.

2.3.2.1 Factors affecting $F_{\text{gas dilution}}$

These are the same as in 2.1.2 above, with the exception of variations to the dilution factor, G_4 , which is covered by V_8 .

2.3.2.2 Factors affecting $F_{\text{volatile particle "dilution"}}$

Factor	Symbol
Nonlinearity affecting the ratio between the high concentration and the low concentration measurements (typically >15,000)	V_1
Alterations to the system flows when the PNC is relocated	V_2
Variations to the inlet concentration between "inlet" and "outlet" measurements (ie source drift)	V_3
Variations in the performance of the diluter between "inlet" and "outlet" measurements (ie diluter drift)	V_4
Presence of non-volatile particles in the source	V_5
Presence of non-volatile particles in the dilution air	V_6
Background particle "noise", ie release of particles from internal walls	V_7
Variations to the particle dilution factor between this determination and the gas dilution factor measurement (due to diluter set-up, drift, variable losses etc)	V_8
Corrections to STP (relative to gas measurement)	V_9

2.3.2 Method 2

$$E_{\text{volatile removal}} = 1 - (C_{\text{PNC}} \cdot F_{\text{gas dilution (heater on)}} / C_{\text{PNC}} \cdot F_{\text{gas dilution (heater off)}}) \quad (6)$$

2.3.1.1 Factors affecting the C_{PNC} ratio

Factor	Symbol
Nonlinearity affecting the ratio between the high concentration and the low concentration measurements (typically >100)	H_1
Presence of non-volatile particles in the source	H_2
Presence of non-volatile particles in the dilution air	H_3
Background particle "noise", ie release of non-volatile particles from internal walls	H_4
Variations to the inlet concentration between "heater off" and "heater on" measurements (ie source drift)	H_5

2.3.2.3 Factors affecting the $F_{\text{gas dilution}}$ ratio

Factor	Symbol
Generic gas dilution ratio errors, to include analyser drift, reproducibility of set up etc	H ₇

In principle this ratio is between two similar measurements of the gas dilution factor. Some of the potential errors (such as uncertainties in the calibration gases) will cancel out.

2.4 Expected Diffusion Losses

Some losses of solid particles (ie penetration efficiencies below 1) are expected because of diffusion of particles to the walls. This applies especially to smaller particles. It is possible to allow for these losses by making use of the measured particle dilution factors. Calculation of the expected losses due to diffusion within the PCMS would need detailed knowledge of the dimensions and arrangement of pipework in the PCMS, and would even then be approximate. As a rule of thumb, typically 10-20 % losses are expected for 30 nm particles in apparatus containing moderately convoluted pipework.

3 Quantification of the factors

3.1 Particle concentration measurement

3.1.1 Factors affecting C_{PNC}

Factor	Symbol	Constraint	Limits	Effect on result	Comment
PNC calibration	C_1	Calibration procedure	10% [1]	10%	An extra 3% error (up to 3,000 cm ⁻³) can arise if coincidence is not corrected for. See A1
PNC drift	C_2	Knowledge of typical drift between 6 monthly calibrations	~5% in 6 months (in NPL's experience)	~5%	Drift between calibrations needs to be monitored
Volatile particles	C_3	1% of volatile particles in size range	number of volatile particles in typical sample	?	This cannot be addressed without more data, but could be significant.
Corrections to STP	C_4	<35°C outlet temperature	In practice between 20 and 35°C	2% (if 27°C is assumed)	Outlet temperature should be checked

3.1.2 Factors affecting $F_{\text{gas dilution}}$

Factor	Symbol	Constraint	Limits	Effect on result	Comment
Gas mixture	G_1	Certification of mixture	2% [1]	2%	
Gas analyser	G_2	Calibration gas; performance checks on analyser	2 ppm [1]	6%	Careful checks on the analyser are needed.
Dilution gas	G_3	Check of dilution gas through NOx analyser	Likely to be < 0.5 ppm	1.5%	Check needs to be incorporated
Set-up variations	G_4	Repeat measurements	Not given	~20% (from ILCE_LD Final Report, with CO gas)	Ideally the gas test would be done on the day of the vehicle measurement. Criteria for repeats, and for retrospective adjustment needed.

3.1.3 Factors affecting the final result

Factor	Symbol	Constraint	Limits	Effect on result	Comment
Low size cut-off	F ₁	Requirements for low size cut-off	50±12% at 23nm and > 90% at 41nm	~5%	Periodic checking of cut-off curve should be required. See A3
Penetration efficiency	F ₂	Allowed limits on penetration efficiency	60% @ 30nm, 70% @ 50nm, 80% @ 100nm	~30%	Incorporation of penetration efficiencies is recommended. See A4

3.2 Particle penetration efficiency

For illustrative purposes the input concentration is assumed to be 5,000 cm⁻³, making the output concentration around 33 cm⁻³, at a dilution factor of 150.

3.2.1 Factors affecting F_{particle dilution}

3.2.1.1 Single PNC

Factor	Symbol	Constraint	Limits	Effect on result	Comment
Nonlinearity	P _{S1}	Linearity check		small	If coincidence errors are not allowed for the effect can be 9%. See A2
Alterations to flow	P _{S2}	Simulation of PNC with mass flow controller	Depend on actual flows	small	
Source drift	P _{S3}	Repeat measurement	Not given	~5%	Acceptable drift needs to be defined
Diluter drift	P _{S4}	Repeat measurement	Not given	~5%	Acceptable drift needs to be defined (combined with P _{S3})
Dilution particles	P _{S5}	Check on dilution gas source	None but say < 1 cm ⁻³	3%	Check should be required
Particle “noise”	P _{S6}	Check on HEPA-fed system	< 1 cm ⁻³	3%	
Set-up variation	P _{S7}	Independent later remeasurement of particle dilution factors	Not given	~15% (from ILCE_LD Final Report)	Criteria for repeats, and for retrospective adjustment needed.
Corrections to STP	P _{S8}	<35°C outlet temperature	In practice between 20 and 35°C	2% (if 27°C is assumed)	Outlet temperature should be checked

3.2.1.2 Dual PNC

Factor	Symbol	Constraint	Limits	Effect on result	Comment
PNC ratio	P _{D1}	Comparison of PNCs	10% on each PNC	14%	Coincidence corrections need to be applied. See A2
Dilution particles	P _{D2}	Check on dilution gas source	None but say $< 1 \text{ cm}^{-3}$	3%	Check not currently required?
Particle “noise”	P _{D3}	Check on HEPA-fed system	$< 1 \text{ cm}^{-3}$	3%	
Set-up variation	P _{D4}	Independent later remeasurement of particle dilution factors	Not given	~15% (from ILCE_LD Final Report)	Criteria for repeats, and for retrospective adjustment needed.
Corrections to STP	P _{D5}	$< 35^\circ\text{C}$ outlet temperature	In practice between 20 and 35°C	2% (if 27°C is assumed)	Outlet temperature should be checked

3.3 Volatile particle removal efficiency

3.3.1 Method 1: Factors affecting $F_{\text{volatile particle “dilution”}}$

Factor	Symbol	Constraint	Limits	Effect on result	Comment
Nonlinearity	V ₁	Linearity check		Small (with coincidence correction)	Coincidence corrections need to be applied. See A2
Flow alterations	V ₂	Simulation of PNC with mass flow controller		small	
Source drift	V ₃	Repeat measurement	Not given	~5%	Acceptable drift needs to be defined
Diluter drift	V ₄	Repeat measurement	Not given	~5%	Acceptable drift needs to be defined
Source particles	V ₅	Check only necessary if overall criterion is not met			Contamination should be checked if a problem is seen
Dilution particles	V ₆	Check on dilution gas source	None but say $< 1 \text{ cm}^{-3}$	>50%	Check only necessary if overall criterion is not met
Particle “noise”	V ₇	Check on HEPA-fed system	$< 1 \text{ cm}^{-3}$	>50%	Check only necessary if overall criterion is not met

Set-up variations	V ₈	Repeat measurements	Not given	~15%	Check only necessary if overall criterion is not met
Corrections to STP	V ₉	<35°C outlet temperature	In practice between 20 and 35°C	2% (if 27°C is assumed)	Outlet temperature should be checked

3.3.2 Method 2: Factors affecting the C_{PNC} ratio

Factor	Symbol	Constraint	Limits	Effect on result	Comments
Nonlinearity	H ₁	Linearity check		Small	Coincidence corrections need to be applied. See A2
Source particles	H ₂	Check only necessary if overall criterion is not met			Contamination should be checked if a problem is seen
Dilution particles	H ₃	Check on dilution gas source	None but say < 1 cm ⁻³	>50%	Check only necessary if overall criterion is not met
Particle “noise”	H ₄	Check on HEPA-fed system	None but say < 1 cm ⁻³	>50%	Check only necessary if overall criterion is not met
Source drift	H ₅	Repeat measurement	Not given	~5%	Acceptable drift needs to be defined
Set-up variations	H ₆	Independent later remeasurement	Not given	~15%	Check only necessary if overall criterion is not met

Factors affecting the F_{gas dilution} ratio

Factor	Symbol	Constraint	Limits	Effect on result	Comment
Dilution ratio errors	H ₇	Repeat measurements of room temperature / hot dilution ratio	none	? 10%	Acceptable variation needs to be defined

4 Conclusions

In all cases errors of up to 9% are avoided by applying a coincidence correction to the PNC data. This is therefore worthwhile, but care needs to be taken that the coincidence correction is appropriate.

Also in all cases, high dilution factors make the measurements more prone to errors. A dilution factor of around 150 has been assumed here.

The main factors affecting the particle concentration measurements are the PNC calibration (~10%), the validity of the dilution factor used at the time of the measurement (~20%), and particle penetration efficiency (~30%).

The last figure can be reduced to around 15% by using the average particle dilution factor instead of the gas dilution factor for the particle concentration measurements. The 20% estimate may be high as it is based on data when an earlier version of the procedures was being followed.

For particle penetration efficiency measurements, the use of a single PNC for both measurements is generally preferable to the use of two, as the calibration of the PNC cancels out, though this benefit is partially offset by other factors. If a single PNC is used, the main factor appears to be the reproducibility of the VPR as set up for the particle dilution, compared with when it is set up for the gas dilution (~15%). This may also be an overestimate, and could be reduced by carrying out the two measurements in succession without altering the VPR.

For volatile particle removal efficiency measurements, there are potentially large errors in the absolute determination due to the small numbers of particles at the outlet of the VPR. These can be minimised by using Method 2 together with the highest available concentration of volatile particles at the inlet. However, in general VPR performances appear to meet the 99% removal requirement comfortably, and the errors have the effect of reducing the apparent efficiency, so that even quite large errors of this kind do not affect the validity of the result.

5 References

- 1 Amendments to the UNECE Regulations, Regulation No. 83, Proposal for draft supplement 7 to the 05 series of amendments to Regulation No.83, ECE/TRANS/WP.29/GRPE/2007/8.
- 2 Volatile Particle Remover Calibration Procedure ED47382004/VPR Draft Revision 3, July 2007, AEA E&E.

Annexes

A1 PNC calibration

The PNC is calibrated by comparison to a reference standard at 5 or more concentrations [1]. The reference standard in practice is either an aerosol electrometer or another PNC that has previously been calibrated using an aerosol electrometer. The aim of the calibration is to convert the indicated concentration on the PNC into the reference concentration from the aerosol electrometer (or PNC). Part of the procedure to convert the indicated PNC concentration into the ‘correct’ concentration defined by the reference standard is to apply a coincidence correction. The UNECE proposed procedure [1] requires that the agreement is better than 10%, and that the correlation coefficient (R^2) > 0.97.

There are two contributions to the uncertainty in the PNC calibration arising from this procedure:

1. The quoted uncertainty associated with the reference instrument.
2. Any errors associated with the suitability of the coincidence correction algorithm.

The first of these is difficult to reduce, but its effect can be minimised by direct comparison with a calibrated aerosol electrometer, as opposed to comparison with another PNC that has previously been calibrated using the electrometer method due to the propagation of errors. Its value is taken to be 10%.

The data below assumes that the only deviation from a linear PNC response (with respect to the electrometer) is due to coincidence. It assumed that the providers of the calibration service have incorporated effects due to multiply charged particles and differences between sampling lines into their uncertainties.

A common theoretical description of the divergence of the measured and actual number concentrations due to coincidence is given by:

$$C_{\text{actual}} = C_{\text{measured}} \exp(C_{\text{actual}} Q \tau_p) \quad (\text{A1})$$

Where C_{actual} is the actual number concentration, C_{measured} is the number concentration indicated by the PNC, Q is the detector flow rate, and τ_p is the length of a typical pulse in the PNC.

The parameters used for these calculations are for a typical PNC used for these measurements. The effect of coincidence is then shown in the table below:

Actual concentration (P/ccm)	PNC Measured concentration (P/ccm)	Undercount (%)
11000	9945	9.6%
10000	9124	8.8%
9000	8287	7.9%
8000	7434	7.1%
7000	6565	6.2%
6000	5679	5.4%
5000	4776	4.5%
4000	3856	3.6%
3000	2919	2.7%
2000	1964	1.8%
1000	991	0.9%

The table shows that if no coincidence correction is made, underreads of up to 9% are expected at the higher permitted concentrations. These errors are in addition to the uncertainty of the calibration.

A2 Comparability of high and low PNC concentrations

As discussed above, the indicated concentrations from the PNC do not scale linearly with the actual number concentration due to coincidence. If coincidence is not accounted for, the ratios of high and low concentrations will have errors of up to 9%.

If a single PNC is used then the uncertainty in the calibration factors from the two measurements cancels out, leaving only the uncertainty due to coincidence to consider.

If two PNCs are used, then the uncertainties in the calibration factors must also be taken into account.

A3 Low-size cut-off

The detection efficiency cut-off region of the PNC overlaps with typical particle size distributions obtained from PMP measurements. This means that any variation in the cut-off characteristics of the PNC will result in a change in the measured concentration. The quantity being measured can be described by:

$$C_{\text{inlet}} = \int_{d_{\text{CPCmin}}}^{d_{\text{cyclone cut}}} E_{\text{PNC}}(d) \times F_{\text{particle concentration}}(d) \quad (\text{A2})$$

Using this relationship, we can estimate the effect of varying either the PNC cut-off by simulating both typical size distributions and cut-off curves. For the size distributions, two typical data sets were taken, based on PMP data.

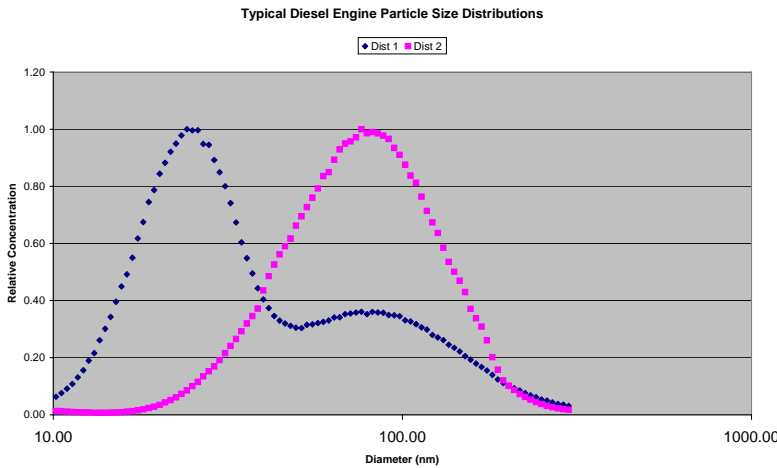


Figure 2: Typical size distributions for diesel engine exhaust.

For the PNC cut-off, a polynomial fit of some typical PNC cut-off behaviour data was used. To simulate the extreme case of PNCs that only just meet the D_{50} specification, two more limiting case cut-off curves were derived, as shown in Figure 3.

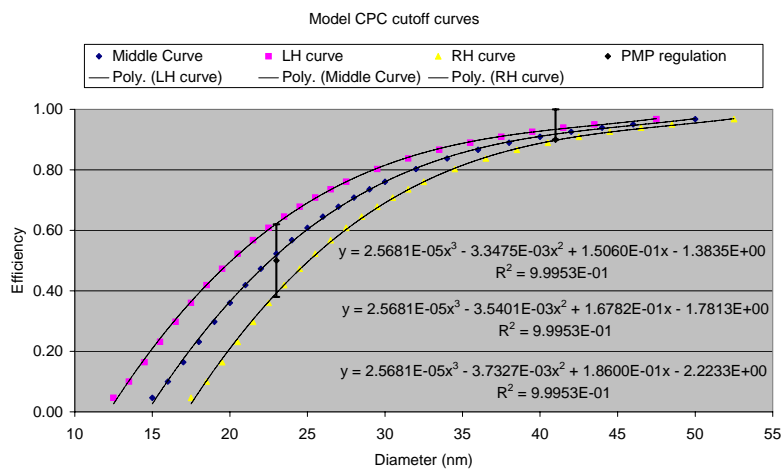


Figure 3: Simulated PNC cut-off curves used.

Equation A2 was evaluated for every combination of cut-off curve and size distribution and the relative change in PNC signal obtained. For the bimodal distribution, the PNC signal was found to vary by up to 8.5% when shifting from the central distribution to either extreme. For the monomodal distribution, this variation decreases to <1%.

Making the crude estimate that the size distributions will each feature for around half the time, we estimate that the errors arising from a lack of comparability in the cut-off curves of the PNCs would be around 5%.

A4 Correction for penetration efficiency

Plots of the cumulative integrals of the two typical size distributions shown in A3, multiplied by a typical PNC cut-off curve, are given in Figure 4.

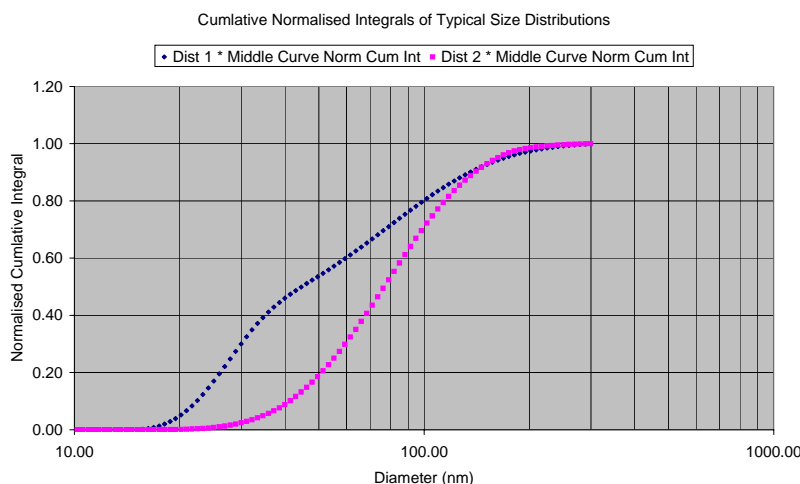


Figure 4: Cumulative measured particle numbers for two typical size distributions.

From these curves, the proportions of particle numbers in three relevant size categories are approximately:

Distribution	20-40 nm “30 nm”	40-70 nm “50 nm”	>70 nm “100 nm”
1	50%	20%	30%
2	10%	30%	60%

If we assume that the penetration efficiencies in the three size categories are the minimum allowed, ie 60, 70 and 80% respectively, the errors due to the gas dilution factor being used will be around 32% for Distribution 1 and 25% for Distribution 2. These will therefore be the differences in measured data between an ideal system and one with the minimum allowed performance. We therefore estimate that the variation in reported results when different systems are used but no allowance is made for penetration efficiency is around 30%.

If, alternatively, a particle dilution factor is used instead of the gas dilution factor, differences between different systems will depend on the accuracy of the particle dilution factors used, and on the validity of the method for incorporating the three values into a single “effective” particle dilution factor. Based on the cumulative distributions above, we would propose that the values for 30 nm, 50 nm and 100 nm particle dilution factors are simply averaged. We estimate that variations in reported results from different systems would then be around 15%.