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Report

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Particle Measurement Programme –

Analysis of Errors

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and
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Richard Gilham and Paul Quincey

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By Dr Stuart Windsor, Business Leader, Analytical Science Team

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EXECUTIVE SUMMARY

This document has been prepared for the Department for Transport (DfT) as part of the Particle Measurement Programme (PMP). The aim of the 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. These requirements and procedures [1-3] were themselves being modified during the time that this document was being written, to some extent in response to its early drafts. This final document takes into account changes agreed at the PMP meetings at DfT on 8th and 9th October 2007.

A provisional rough estimate of the uncertainty for particle concentration measurements, based on the figures and assumptions used here, is 15%. This uncertainty figure corresponds to a level of around 95% confidence. It should be emphasised that it is not possible to be fully rigorous or definitive, because there will be variations in how the methods are carried out in practice, and some of the factors are not well characterised. Nevertheless, this should be a realistic approximate figure.

The major factors are the calibration of the particle number counter (PNC), an area where it is acknowledged that international standardisation is required, and the reproducibility of the Particle Conditioning and Measuring System (PCMS).

The error calculation applies when total dilution factors of 150 are used. In all cases, high dilution factors make the measurements more prone to errors, because the actual particle dilution factor is more difficult to determine. When a dilution factor around 600 is used, for example with a Gasoline Direct Injection (GDI) engine, additional care would be required to ensure that statistical variations, and the effects of leakage and “noise”, were addressed during the dilution factor measurement. Similar uncertainties could still be obtained.

It is important that significant factors such as reproducibility and test source stability are properly quantified and controlled within the procedures. Consideration should be given to retrospective correction of data using subsequent calibration results.

Although more than 99% of volatile particles are removed by the Volatile Particle Remover (VPR), the presence of a 1% fraction of the volatile particles emitted by the vehicle could have a significant influence on results, but this effect is not investigated in detail here.

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 the hot/cold method 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 results.

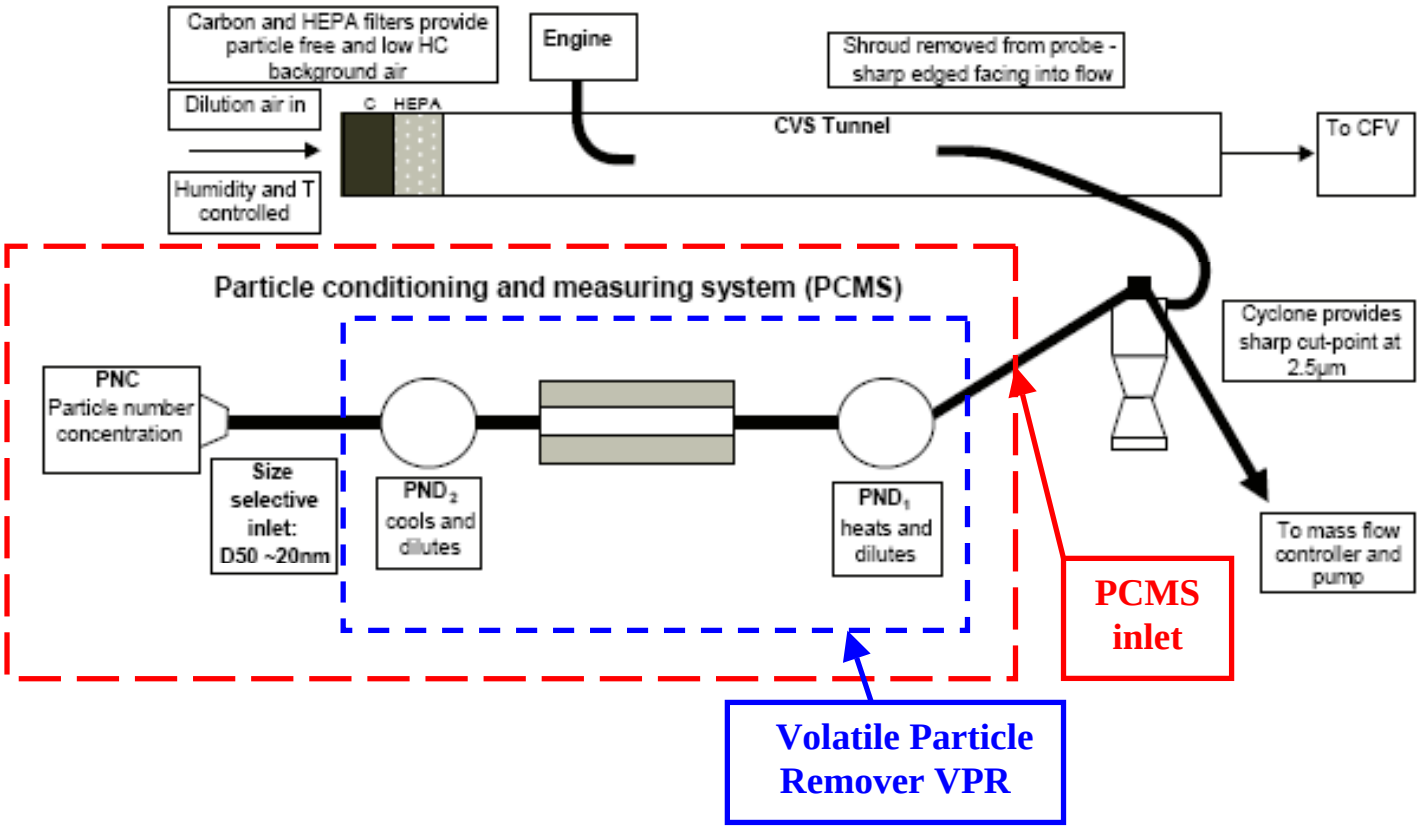

Figure 1: Schematic diagram of the measurement system

1 Introduction, Scope and Approach

1.1 Background

This document has been prepared for the Department for Transport (DfT) as part of the Particle Measurement Programme (PMP). PMP is a collaborative research programme under the auspices of the UN-ECE, chaired by DfT, aimed at developing robust measurement procedures for vehicle particle emissions.

The aim of the 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. These requirements and procedures [1-3] were themselves being modified during the time that this document was being written, to some extent in response to its early drafts. This final document takes into account changes agreed at the PMP meetings at DfT on 8th and 9th October 2007.

1.2 Scope

Before analysing the uncertainties of a measurement, it is important to clarify what we are trying to measure. The system under consideration is limited to the Particle Conditioning and Measuring System (PCMS), outlined in the red outer 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 below. In practice the PCMS dilutes the air stream before the number concentration is measured at the Particle Number Counter (PNC), to bring concentrations into the counting range of 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 dilution factor is more properly called the Particle Concentration Reduction Factor, because reduction beyond simple dilution is involved, but is referred to as the particle dilution factor here. The elements that dilute the sample and remove the volatile particles are together labelled the Volatile Particle Remover (VPR), the blue inner dashed box in Figure 1.

The UNECE proposed procedure [1] allows total dilutions between 100 and 3,000 (10 to 200 on PND_1 combined with 10 to 15 on PND_2). This report primarily considers total dilution factors of around 150, a typical value when measuring post-Diesel Particulate Filter (DPF) emissions. The analysis will also generally assume that the airstream to be measured contains typical post-DPF particle distributions.

The report will also comment on the situation when total dilution factors are around 600, a typical value for Gasoline Direct Injection (GDI) exhaust measurements.

Two separate measurements are considered here:

1.2.1 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 test 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 at the PCMS inlet 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, typically < 10,000 cm^{-3}.

With a total dilution factor of 150, 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. The procedure for determining this parameter is given in [3]. 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 currently agreed approach for the particle concentration measurement uses the basic measurement equation:

$$C_{inlet} = C_{PNC} \times F(av)_{particle\ dilution} \qquad (1)$$

where C_{PNC} is the number concentration measured by the PNC and F(av) is the simple average of the three particle dilution factors obtained at 30 nm, 50 nm and 100 nm. These are determined at the VPR dilution and heating settings to be used for the vehicle measurements, by the method described in [2].

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 Draft VPR Calibration Procedure [2] requires the concentration of the test particles for particle dilution factor measurements to be between 5,000 and 10,000 cm^{-3}. With a dilution factor of 150, the downstream concentrations are therefore 33 to 66 cm^{-3}.

1.2.2 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 proportion of volatile particles of a specified type 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 previous one in that an accurate evaluation is only required if the proportion removed is close to the required minimum (99%). If, as is generally the case, the proportion removed is significantly higher than this, the measurement becomes more of a validation check.

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

The basic measurement equation for Method 1 is:

$$E_{\text{volatile removal}} = 1 - (F(av)_{\text{particle dilution}} / F_{\text{volatile particle "dilution"}}) \qquad (2)$$

where $F_{\text{volatile particle "dilution"}}$ is the particle dilution factor for the tetracontane particles.

The VPR calibration procedure [2] specifies a volatile particle concentration of >10,000 cm^{-3}. With a dilution factor of 150 and a removal efficiency of 99%, the downstream concentration will be >0.7 cm^{-3} – a value too low 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:

$$E_{\text{volatile removal}} = 1 - (C_{PNC}\,(\text{heater on}) / C_{PNC}(\text{heater off})) \qquad (3)$$

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 cm^{-3} and ~ 0.7 cm^{-3}. These values can be increased by having an input concentration much higher than 10,000 cm^{-3} (which does not need to be measured).

It is acknowledged that the two methods are not expected to give exactly the same answer, due to the heater affecting losses of non-volatile as well as volatile particles, but it is expected that the two methods will each be fit for purpose.

1.3 Approach

There are several different approaches to uncertainty analysis and this report is based on that of the ISO Guide to the Expression of Uncertainty in Measurement (GUM) [4]. In this approach, you:

(1) define an equation that is used to produce the result from various input measurements and parameters;

(2) identify the various operational factors that influence the result, based on a practical understanding of the measurement process;

(3) quantify the uncertainty in each of these factors;

(4) evaluate the effect of each of these uncertainties on the result by how each factor features in the equation; and

(5) combine the effects of all the factors, typically by adding them in quadrature (ie taking the square root of the sum of their squares).

Within this document, the equations in (1) are defined in Section 1.2 above; the factors (2) are identified in Section 2; the uncertainty in each factor (3) and its effect on the final result (4) are given by the "Limits" and "Effect on result" columns respectively in Section 3; and the combination of effects (5) is given in Section 4.

2 Factors affecting the measurements

The tables below are meant to help focus on the factors that affect the 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

$$C_{inlet} = C_{PNC} \times F(av)_{particle\ dilution} \qquad (1)$$

2.1.1 Factors affecting C_{PNC}

Factor	Symbol
PNC number concentration calibration accuracy - 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 ~5,000 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 $F_{particle\ dilution}$

The determination of $F_{particle\ dilution}$ 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 particle counting system may not be suitable for particles close to 30 nm in size. Either one or two PNCs that are suitable for measuring particles of this size are needed depending on the method used.

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 $F_{particle\ dilution}$ is taken here to be 150, so that a typical concentration after the VPR is 33 to 66 cm^{-3}. In practice the dilution factors must be measured at the full range of dilution settings that are to be used.

2.1.2.1 Single PNC

Factor	**Symbol**
Nonlinearity affecting the ratio between the high concentration and the low concentration measurements (typically 150)	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 vehicle emission measurement (due to diluter set-up, drift, variable losses etc)	P_{S7}

2.1.2.2 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 vehicle emission measurement (due to diluter set-up, drift, variable losses etc)	P_{D4}

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 taking a simple average of the particle dilution factors	F_2

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

The factors are shown schematically on the fishbone diagrams below.

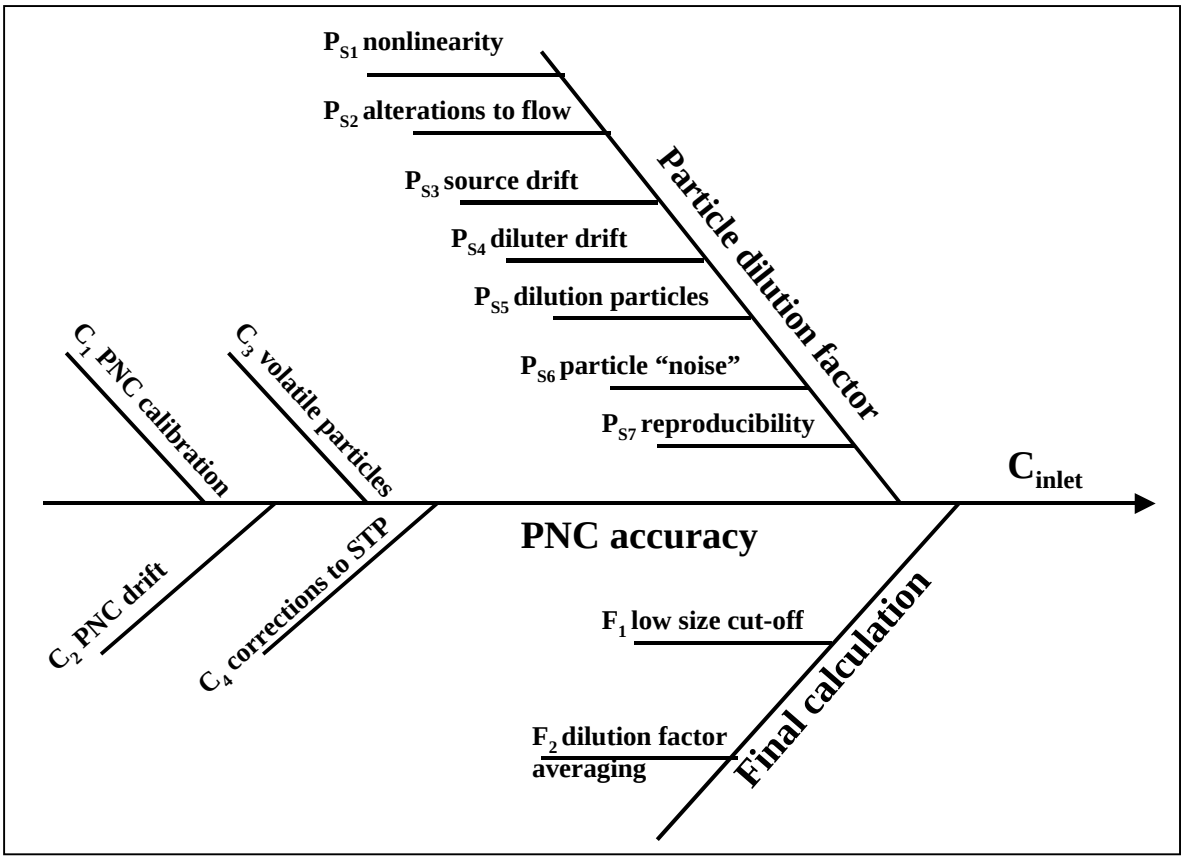

Figure 2: Fishbone diagram for particle number concentration measurements with a single PNC for the dilution factor measurement

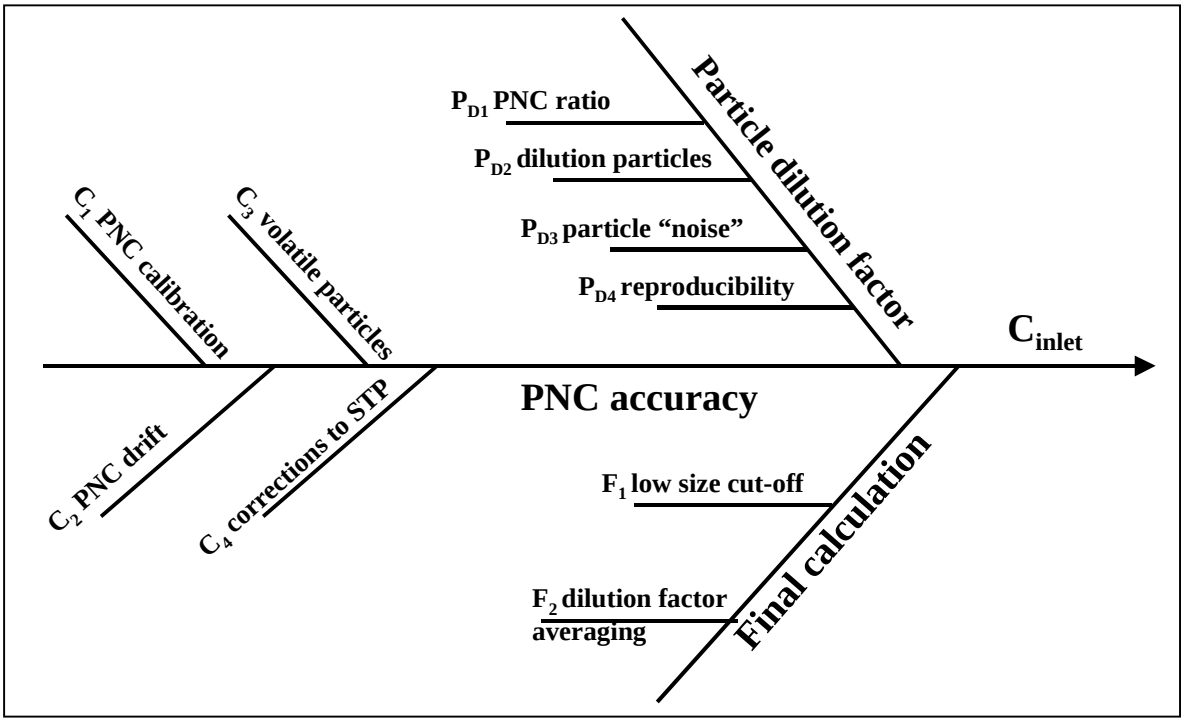

Figure 3: Fishbone diagram for particle number concentration measurements with dual PNCs for the dilution factor measurement

2.2 Volatile particle removal efficiency

2.2.1 Method 1

$$E_{\text{volatile removal}} = 1 - (F(av)_{\text{particle dilution}} / F_{\text{volatile particle "dilution"}}) \qquad (2)$$

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 (C_{40}) particles of around 30 nm diameter, and the comparison of this with the particle 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.

2.2.1.1 Factors affecting $F(av)_{\text{particle dilution}}$

These are the same as in 2.1.2 above, with the exception of variations to the dilution factor, P_{S7} and P_{D4}, which are covered by V_8.

2.2.1.2 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 non-volatile particle dilution factor between this determination and the non-volatile particle dilution factor measurement (due to diluter set-up, drift, variable losses etc)	V_8

2.2.2 Method 2

$$E_{\text{volatile removal}} = 1 - (C_{PNC}\,(\text{heater on}) / C_{PNC}(\text{heater off})) \quad (3)$$

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

The factors are shown schematically on the fishbone diagrams below.

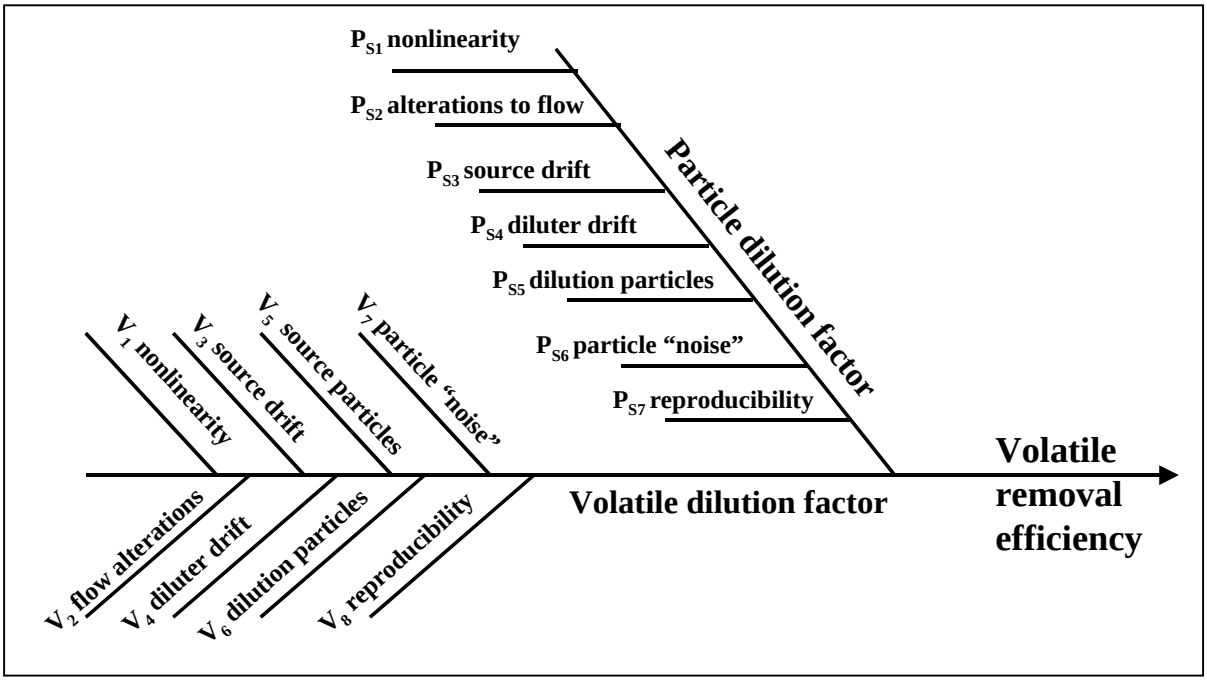

Figure 4: Fishbone diagram for volatile particle removal efficiency measurements with Method 1

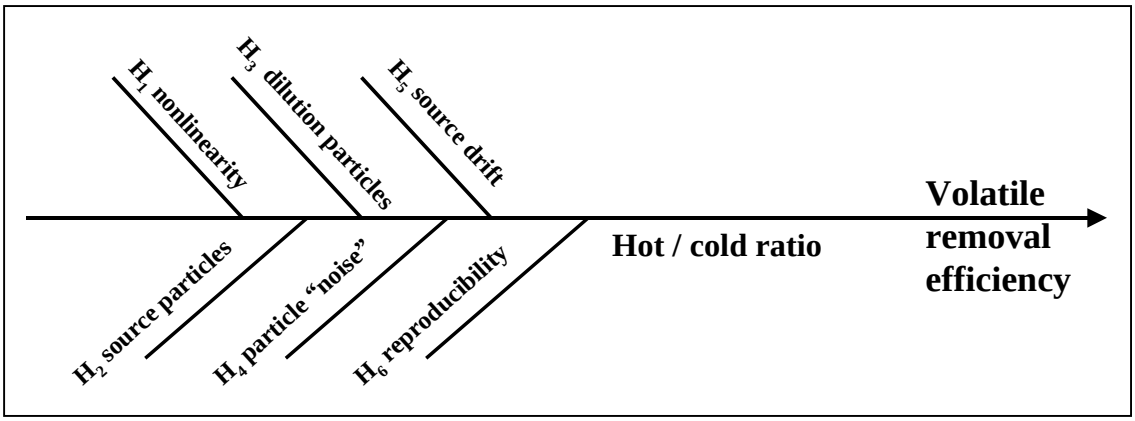

Figure 5: Fishbone diagram for volatile particle removal efficiency measurements with Method 2

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 [3]	10% [1]	10%	The details of the calibration procedure are important. 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 should 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 $F_{particle\ dilution}$

3.1.2.1 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 HEPA-fed system	< 0.5 cm^{-3}	~1.5%	
Particle "noise"	P_{S6}	Stable zero check	< 0.2 cm^{-3}	Small	
Reproducibility	P_{S7}	Independent later remeasurement of particle dilution factors	Not given	~10% (to be evaluated in trials)	Criteria for repeats, and for retrospective adjustment needed.

3.1.2.2 Dual PNC

Factor	Symbol	Constraint	Limits	Effect on result	Comment
PNC ratio	P_{D1}	Comparison of PNCs	Comparability of the calibration corrections applied to the two PNCs	~5%	Coincidence corrections need to be applied. See A2
Dilution particles	P_{D2}	Check on HEPA-fed system	< 0.5 cm^{-3}	1.5%	
Particle "noise"	P_{D3}	Stable zero check	< 0.2 cm^{-3}	small	
Reproducibility	P_{D4}	Independent later remeasurement of particle dilution factors	Not given	~10% (to be evaluated in trials)	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	~1%	See A3
Dilution factor average	F_2	None		~9%	See A4

3.2 Volatile particle removal efficiency

3.2.1 Method 1: Factors affecting $F_{volatile\ particle\ "dilution"}$

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 (combined with V_3)
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 HEPA-fed system	< 0.5 cm^{-3}	>50%	Check only necessary if overall criterion is not met
Particle "noise"	V_7	Stable zero check	< 0.2 cm^{-3}	>25%	Check only necessary if overall criterion is not met
Reproducibility	V_8	Repeat measurements	Not given	~15%	Check only necessary if overall criterion is not met

3.2.2 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 HEPA-fed system	< 0.5 cm^{-3}	>50%	Check only necessary if overall criterion is not met
Particle "noise"	H_4	Stable zero check	< 0.2 cm^{-3}	>25%	Check only necessary if overall criterion is not met
Source drift	H_5	Repeat measurement	Not given	~5%	Acceptable drift needs to be defined
Reproducibility	H_6	Independent later remeasurement	Not given	~15%	Check only necessary if overall criterion is not met

4 Conclusions

A provisional estimate of the uncertainty for particle concentration measurements, based on the figures and assumptions used here, is 15% whether using the single or dual PNC method. This figure is obtained by taking the square root of the sum of the squares for the individual "Effect on result" components in each case, and rounding to the nearest 5% to reflect the approximate nature of the results. This uncertainty figure corresponds to a level of around 95% confidence. It should be emphasised that it is not possible to be fully rigorous or definitive, because there will be variations in how the methods are carried out in practice, and some of the factors are not well characterised. Nevertheless, this should be a realistic approximate figure.

The major factors are the calibration of the PNC, an area where it is acknowledged that international standardisation is required, and the reproducibility of the PCMS. PNC calibration is discussed further in Annex A1. Additional errors of up to 9% can be introduced if an appropriate coincidence correction is not applied to the PNC data.

The inaccuracy in the result due to taking a simple average of the 30nm, 50nm and 100nm dilution factors, though potentially significant at up to 9%, has not been included in the total as the calculation would be applied with the same consequences by all laboratories.

The figures apply when total dilution factors of 150 are used. In all cases, high dilution factors make the measurements more prone to errors, because the actual particle dilution factor is more difficult to determine. When a dilution factor around 600 is used, for example with a GDI engine, additional care would be required to ensure that statistical variations, and the effects of leakage and "noise", were addressed during the dilution factor measurement. Similar uncertainties could still be obtained. This is discussed further in Annex A2.

It is important that significant factors such as reproducibility and test source stability are properly quantified and controlled within the procedures. Consideration should be given to retrospective correction of data using subsequent calibration results.

The presence of the allowed sub-1% fraction of volatile particles emitted by the vehicle could have a significant influence on results, but this effect is not investigated in detail here.

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 results.

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/2008/

2 Volatile Particle Remover Calibration Procedure ED47382004/VPR Draft Revision 3, July 2007, AEA E&E.

3 Particle Number Counter Calibration Procedure ED47382004/PNC Draft Revision 3, July 2007, AEA E&E.

4 ISO Guide to the Expression of Uncertainty in Measurement, ISO, Geneva, 1993

Annexes

A1 PNC calibration

PNC calibration procedures are an active field on international standardisation, for example through ISO TC 24. According to the UNECE Regulations, Regulation No. 83 [1], the PNC is calibrated by comparison to a reference standard at 6 or more concentrations. 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 as described is to demonstrate agreement, within stated limits, between the PNC and the reference standard and to apply the best available correction to the instrument. Coincidence corrections to PNCs at higher concentrations (typically > 5,000 cm^{-3}) are also required. The UNECE proposed procedure requires that the agreement before correction is better than 10%, and that the Pearson correlation coefficient $R^2 > 0.97$. This is often described as a measure of linearity, though in practice it is a measure of the combination of linearity and the scatter in the results

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

1. The uncertainty associated with the reference instrument (which is currently poorly quantified).
2. The accuracy of the calibration factor used, which will depend on aspects of the calibration procedure other than the uncertainty of the reference instrument.
3. Any errors associated with the suitability of the coincidence correction algorithm.

The first two contributions are difficult to quantify as the uncertainty associated with an aerosol electrometer, or a reference PNC that will have been previously calibrated against an aerosol electrometer, are not well established, but figures of 5-10% are considered reasonable. This assumes 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:

$$C_{\text{actual}} = C_{\text{measured}} \exp\left(C_{\text{actual}} Q \tau_p\right) \qquad \text{(A1)}$$

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/cm^3)	PNC Measured concentration (P/cm^3)	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%

Table 1: Examples of coincidence losses

Table 1 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.

For the purposes of this report, the uncertainty assigned to the PNC calibration, in relation to other independent PNC calibrations, is taken to be 10%.

Issues of low absolute numbers and long averaging times become important at low concentrations. This is discussed briefly in Annex A2.

A2 Comparability of high and low PNC concentrations

The determination of particle dilution factors requires an accurate ratio for 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 mostly cancels out, leaving only the uncertainty due to coincidence, and effects at low concentrations, to consider.

If two PNCs are used, then the uncertainties in the calibration factors must also be taken into account. If they have been corrected to the same calibration system, the factors should again mostly cancel out.

At low concentrations, a number concentration measurement must be taken for a longer period of time than at higher concentrations to yield an acceptable error due to

statistical uncertainty. This is addressed by the requirement for a minimum cumulative sample of 10,000 particles in the revised version of [2]. In such measurements, the optimum measurement period is often a compromise between statistical uncertainty and drift in the analyte being considered.

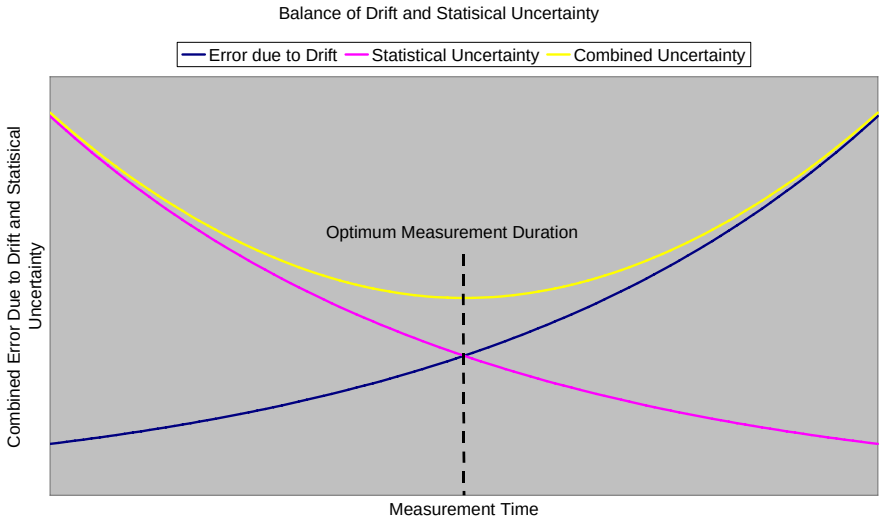

Figure 6: Simple example of the compromise between statistical uncertainty and drift for low concentration measurements.

To quantify errors arising from comparisons of high and low PNC concentration readings, more detail about the drift arising from the aerosol generators used is required.

A3 Low-size cut-off

The detection efficiency cut-off region of the PNC is within the range of 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:

$$C_{\text{inlet}} = \int_{d_{\text{CPC}_{\text{min}}}}^{d_{\text{cyclone cut}}} E_{\text{PNC}}(d) \times F_{\text{particle concentration}}(d) \qquad \text{(A2)}$$

Where E_{PNC} is the detection efficiency at a particular size d and $F_{\text{particle concentration}}$ is the particle number concentration as a function of particle size d.

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, a typical data set was taken, based on PMP data (Figure 7).

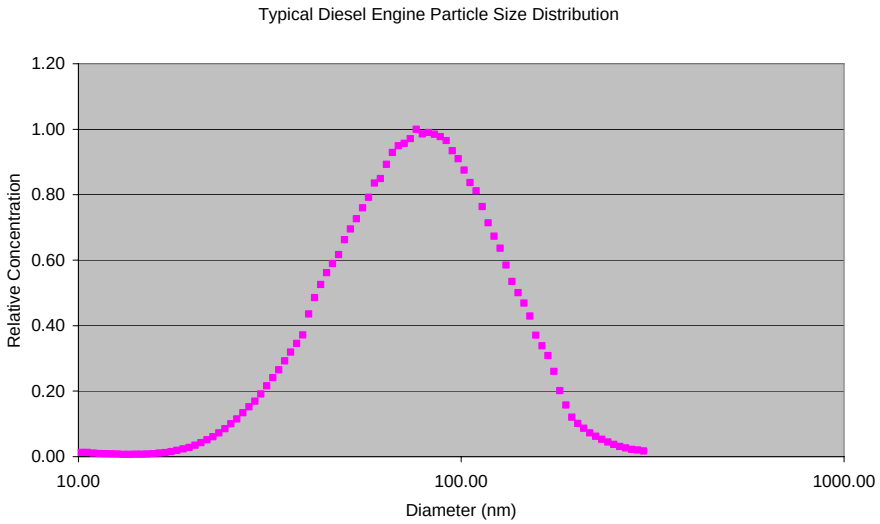

Figure 7: Typical size distribution for diesel engine exhaust.

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 8.

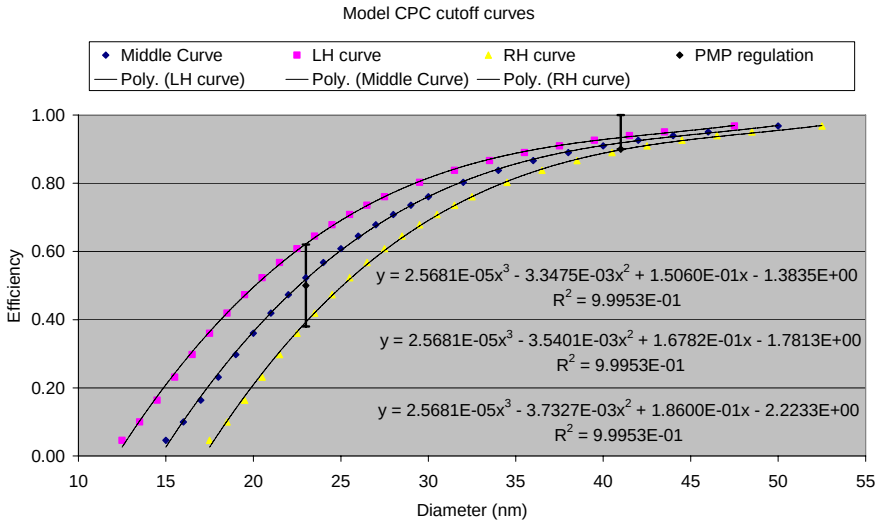

Figure 8: Simulated PNC cut-off curves used.

Equation A2 was evaluated for every combination of cut-off curve and size distribution and the relative change in PNC signal obtained. The variation was less than 1%, the figure used in the Table for F_1.

A4 Averaging of particle dilution factors

A plot of the cumulative integral of the size distribution shown in A3, multiplied by a typical PNC cut-off curve, is given in Figure 9.

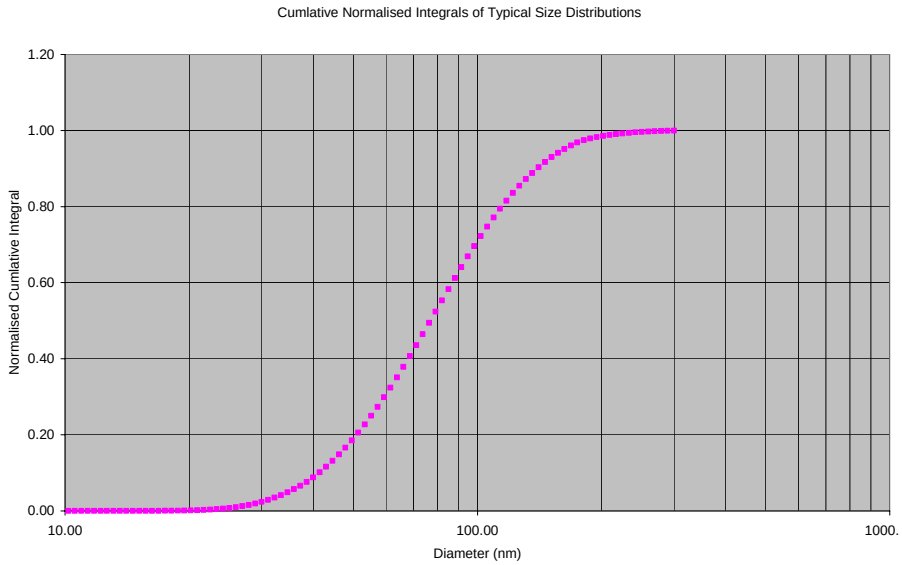

Figure 9: Cumulative measured particle numbers for the typical size distribution.

The proportions of particle numbers in three relevant size categories are approximately:

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

The true value for F(av) in this case should be an average weighted 1:3:6 for the 30nm:50nm:100nm results, rather than the 1:1:1 in the proposed procedures (a simple average). The correct weightings would of course depend on the actual size distribution of the particles being measured.

If we assume that the relative penetration efficiencies in the three size categories are 70, 80 and 100% respectively, in line with the allowed limits [1], the effective penetration efficiency would here be taken to be 83.3% instead of 91%. The errors due to the simple averaging would therefore be around 9%.