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Intercomparison between the TEOM analyser and the European reference sampler for the determination of PM$_{10}$ concentrations

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1. Introduction

The First Daughter Directive 1999/30/EC (DD1) sets Limit Values for particles (PM_{10}) based on measurements performed using the reference method or equivalent. The reference method is defined in the CEN standard EN12341, and is a filter-based gravimetric sampler, which relies on determining the mass of particles collected on a filter after a known volume of air has been drawn through it. Within the UK networks, PM10 monitoring is largely founded on the Tapered Element Oscillating Microbalance (TEOM) analyser.

EN12341 sets out procedures for determining whether non-reference samplers are equivalent to the reference method. However, the procedure is not suitable for determining the equivalence of automatic analysers (such as the TEOM), and the criteria are not directly comparable with the Data Quality Objectives.

A draft EC Guidance Document on Equivalence has the general aim of determining whether a candidate method (including automatic analysers) can be considered equivalent to the reference method. This is broadly defined in terms of whether the candidate method is capable of fulfilling the Data Quality Objectives as specified in the relevant Daughter Directive. It is expected that the equivalence procedure in this document will replace EN12341 in the near future.

An intercomparison exercise using co-located reference samplers and TEOM analysers has been ongoing in the UK since 1999. This report evaluates these data based on the general approach specified in the Guidance Document. Whilst the intercomparison exercise to date does not fulfil the exact requirements for the Field Test procedure defined in the Guidance Document, the results provide a useful indication of how the TEOM analysers might be expected to perform, and informs the requirements for any future work.

2. Description of monitoring sites

Collocated measurements of PM_{10} with TEOM and Kleinfiltergerat are available for the following sites.

-   Belfast Centre: *Urban Background*

The site is located within a pedestrianised area of the city centre. The nearest road is approximately 15 metres from the site and provides access for goods deliveries only. The surrounding area is built-up with business and retail premises (typically 5 storeys high) creating street canyons.

-   Glasgow Centre: *Urban Background*

The site is located within a pedestrianised area of the city centre. The nearest road is approximately 20 metres distance from the site and used for commercial access with an average traffic flow of 20,000 vehicles per day. The surrounding area is open with city centre business and retail premises bordering on three sides.

-   Harwell: *Rural*

The site is located within the grounds of Harwell Science Centre surrounded by large open spaces encompassing agricultural land. The nearest road is for access to buildings on the site only and is approximately 300 metres away. Little or no traffic uses the access road.

-   Marylebone Road: *Kerbside*

The site is located on the kerbside of a busy arterial route in central London with an average traffic flow of 90,000 vehicles per day. The surrounding area forms a street canyon.

- <u>Port Talbot</u>: *Industrial*

The site is located within the grounds of a small hospital. The nearest road is 75 metres from the site (average traffic flow of 50,000 – 55,000 vehicles per day on weekday). The site is approximately 700 metres from a large steelworks, which is known to contribute to local levels of pollution.

- <u>Thurrock</u>: *Urban Background*

The site is located within an existing building approximately 35 metres from the kerbside of the nearest road (average traffic flow of about 9,000 vehicles per 12-hour). The surrounding area is generally open with local light industry.

3. Monitoring equipment

Reference sampler – kleinfiltergerat (KFG)

EN12341 defines three reference samplers for the measurement of PM_{10}. This study has been based on the use of the Low Volume Sampler (LVS) which operates at a flow rate of 2.3 $m^3.h^{-1}$. The PNS-X8 version of the LVS was used, which provides up to 8 days unattended monitoring via 8 independent PM_{10} inlets. The LVS sampler is commonly referred to as the 'kleinfiltergerat' or KFG, and is notated as such in the remainder of this report.

Quartz fibre filters (Whatman QMA 47 mm diameter filters) were used throughout this study for the collection of particulate matter. Pre-conditioning and post-conditioning of filters was undertaken in accordance with the general requirements of EN 12341. Following completion of the sampling cycle (7 days) the filters were stored locally in a fridge before postal despatch to the weighing laboratory. On receipt at the laboratory, filters were equilibrated for a period of at least 48 hours within an air-conditioned weighing room at a temperature of 20°C and a relative humidity of 50% before weighing on a balance with a resolution of 10 μg.

PM_{10} concentrations reported by the KFG are at ambient temperature and pressure, consistent with the requirements of DD1.

Candidate sampler – TEOM

The Tapered Element Oscillating Microbalance (TEOM) has been operating in the UK networks for more than 10 years. The particle mass is determined by continuous weighing of particles deposited onto a filter. The filter is attached to a vibrating hollow tapered glass element. The frequency of mechanical oscillation of this element is a function of its mass. Deposition of particles on the filter leads to changes in the mass of the element and results in changes of its frequency of oscillation. A microprocessor directly converts the vibration frequency to mass concentrations.

The flow rate through the analyser is controlled using thermal mass flow controllers and is automatically measured to determine the mass concentration. Air at 16.67 L min^{-1} is sampled through the sampling head and divided between the filter flow (3 $L.min^{-1}$) and an auxiliary flow (13.67 $L.min^{-1}$). The inlet is heated to 50°C prior to particles being deposited onto the filter in order to eliminate the effect of condensation or evaporation of particle water. An impactor is used as a size-selective inlet for PM_{10}.

PM_{10} concentrations measured by the TEOM are corrected to STP conditions (293K, 101.3 kPa)

4. Data included in this study

A summary of KFG data used in this study is described in Table 1, and the summary of paired data described in Table 2.

Table 1: Summary of sampling periods of Kleinfiltergerat. N is the number of data available

Site	Commencement of sampling	End of sampling	N
Belfast	7 Feb. 2001	7 Sept. 2002	450
Glasgow	2 Dec. 1999	30 Sept. 2002	660
Harwell	29 May 1999	16 Sept. 2002	915
Marylebone Road	3 June 1999	16 Oct. 2002	930
Port Talbot	3 Sept. 1999	11 Sept. 2002	765
Thurrock	27 May 1999	26 Sept. 2002	759

Table 2: Number of data available and paired data included in the comparison

	KFG data	TEOM[1] data	Paired data[2]
Belfast	450	439	372
Glasgow	660	856	571
Harwell	915	1023	800
Marylebone Road	930	961	834
Port Talbot	765	930	675
Thurrock	759	816	612
Total	4479	5025	3864 including 2777 values above 15 µg.m^{-3}

1 Daily mean TEOM concentrations have not been calculated for days in which hourly concentrations are missing

2. Paired data relate to the number of days on which coincident data are available.

5. Outline of approach in the Guidance Document

The method of the "Field Test programme" described in Guidance Document has been used. The general requirements of the field test programme are as follows:

(i) A minimum of 4 comparisons or tests shall be performed.

(ii) Test sites shall be representative for typical conditions for which equivalence will be claimed, including:
- possible episodes of high concentrations,
- episodes of high and low fractions of semi-volatile particles to cover the maximum impact of losses of semi-volatiles,
- episodes of high and low air humidity and temperature to cover any conditioning losses of semi-volatiles during the sampling process,
- episodes of high and low wind speed to cover any dependency of instrument's inlet performance.

(iii) A minimum of 40 measurements averaged over a 24-hours shall be collected for each test.

(iv) Samplers and instruments shall be positioned in such a way that the effect of spatial inhomogeneity of the compound concentration in the sampled air is negligible in comparison with other uncertainty contributions.

(v) Both methods shall be operated under conditions reflecting practical application in the field, e.g., calibration intervals, flow checks, analysis of blank samples.

(vi) Of the full dataset at least 20% of the results shall be greater than or equal to the upper assessment threshold (30 ug/m³) specified in DD1.

(vii) Field tests shall be performed in which Candidate and Reference Methods are compared side-by-side in order to assess:
- the "between-sampler/instrument" uncertainty of the Candidate and Reference Methods *(1)*,
- the "comparability" of the Candidate and Reference Methods *(2)*.

Both will be used in the calculation of the "Combined Uncertainty" to be assigned to the Candidate Method *(3)* and in the determination of the "Expanded Uncertainty" of the Candidate Method *(4)*. The latter is used for comparison to the data quality objective for measurement uncertainty stated in DD1.

5.1. Determination of the uncertainty of the Reference and Candidate Methods

The "between-instrument" uncertainties shall be determined through the use of two collocated samplers. These are calculated from the differences of all 24-hour results of the candidate samplers (or reference samplers) operated in parallel according to the following formula.

$$u_{bs}^2 = \frac{\sum_{i=1}^{n}(y_{i,1} - y_{i,2})^2}{2n}$$

where

$y_{i,1}$ and $y_{i,2}$ are the results of parallel measurements for a single 24-hour period (i)

n = number of 24-hour measurement results.

For the Reference Method, the "between-instrument" uncertainty is required to be less than or equal to 1 μg.m⁻³; For the Candidate Method, the "between-instrument" uncertainty is required to be below 2 μg.m⁻³.

The "between-sampler/instrument uncertainty" shall be determined for each of the comparisons separately, for all results together, for two datasets obtained by splitting the full dataset according to PM concentrations: greater than or equal to, or below 50% of the upper assessment threshold specified in DD1.

5.2. Calculation of the uncertainty due to the "lack of comparability" between Candidate and Reference Methods

For the evaluation of the uncertainty due to the "lack of comparability" between Candidate and Reference Methods it is assumed that the relationship between both methods can be described by a linear relation of the form:

$$y_i = a + bx_i$$

The relation between the results of the Candidate Method and those of the Reference Method is established using a regression technique that leads to a symmetrical treatment of both variables. An orthogonal regression (Major Axis) is advocated.

The general relationship[1] describing the dependence of $u_{c\text{-}s}$ on x_i is given by:

$$u^2_{c-s}(x) = u^2_{ref} + \frac{RSS}{(1+b^2)(n-2)} + \left[\frac{a+(b-1)x}{2}\right]^2$$

where:
- b is the slope from orthogonal regression analysis

$$b = \frac{S_{yy} - S_{xx} + \sqrt{(S_{yy} - S_{xx})^2 + 4S_{xy}^2}}{2S_{xy}}$$

$$S_{xx} = \sum (x_i - \bar{x})^2$$

$$S_{yy} = \sum (y_i - \bar{y})^2$$

$$S_{xy} = \sum (x_i - \bar{x})(y_i - \bar{y})$$

where $\bar{x} = \dfrac{\sum_i x_i}{n}$ and $\bar{y} = \dfrac{\sum_i y_i}{n}$ are the arithmetic means

- a is the intercept from orthogonal regression analysis

$$a = \bar{y} - b \cdot \bar{x}$$

- RSS is the sum of square residuals resulting from the orthogonal regression

$$RSS = \sum_i (y_i - a - b \cdot x_i)^2$$

- k is a coverage factor used to calculate the expanded uncertainty. $k = 2$ for > 32 data pairs

$$RSS = \sum_i (y_i - a - b \cdot x_i)^2$$

- u_{ref} is the random uncertainty of the reference method; the value of u_{bs} calculated for the application of the Standard Method in these tests may be used, supplemented with a contribution for uncovered contributions of $\pm 1 \mu g.m^{-3}$.

- n is the number of data pairs

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[1] Amendment proposed by the WG on 9 December 2003.

The uncertainty u_{C_S} is calculated for each of the comparisons separately, for all results together, and for a dataset representing PM concentrations greater than or equal to 50% of the upper assessment threshold specified in DD1.

5.3. Calculation of the "Combined Uncertainty" to be assigned to the Candidate Method

For all datasets the "Combined Relative Uncertainty" of the Candidate Method $w_{c,CM}$ is calculated by combining the contributions found in *(1)* and *(2)* as follows:

$$w_{c,CM}^2(y_i) = \frac{u_{bs,CM}^2, + u_{C\_S}^2(y_i)}{y_i^2}$$

For each of the datasets the uncertainty at the daily limit value w_{CM} is calculated by taking as y_i the concentration at the limit value:

$$y_i = 50 \ \mu g.m^{-3}$$

5.4. Calculation of the "Expanded Uncertainty" of the Candidate Method

For each of the datasets the "Expanded Relative Uncertainty" of the results of the Candidate Method is calculated by multiplying $w_{c,CM}$ by a coverage factor k reflecting the appropriate number of degrees of freedom resulting from the determination of $w_{c,CM}$ as

$$W_{CM} = k \cdot w_{CM}$$

k=2, where a large number of experimental results are available.

5.5. Criteria for determining equivalence

W_{CM} is compared to the data quality objective for measurement uncertainty (i.e. 25%);

$W_{CM} \leq 25\%_o$: the Candidate Method meets the DQO for measurement uncertainty;

$W_{CM} > 25\%$: the Candidate Method does not meet the DQO for measurement uncertainty.

5.6. Application of correction factors or terms

When a value for *b* outside the range 0.9 to 1.1 is observed, it is permitted to apply a correction factor or term resulting from the regression equation obtained for the full dataset. The corrected values obtained shall satisfy the requirements for all datasets or subsets.

There are three situations:

    (1) The slope is not significantly different from 1, but the intercept is significantly different from 0

    (2) The slope is significantly different from 1, but the intercept is not significantly different from 0

    (3) The slope is significantly different from 1 and the intercept is significantly different from 0

In Case (1) the value of the intercept may be used to correct all input values y_i ($y_{i,\,corr} = y_i - a$). In Case (2), the value of the slope b may be used to correct all input values y_i ($y_{i,\,corr} = y_i/b$). In Case (3), either a term (Case 1) or a factor (Case 2) may be chosen to correct all input values y_i. It is not permitted to apply a correction based on both the term and the factor.

A new relationship is calculated using the resulting $y_{i,\,corr} = c + dx_i$

U_{c-s} is then calculated as:

whether Case (1)
$$u^2_{\,c-s}(y_{corr}) = u^2_{\,ref} + \frac{RSS}{(1+d^2)(n-2)} + \left[\frac{c+(d-1)x}{k}\right]^2 + \mathrm{var}(a)$$

whether Case (2)
$$u^2_{\,c-s}(y_{corr}) = u^2_{\,ref} + \frac{RSS}{(1+d^2)(n-2)} + \left[\frac{c+(d-1)x}{k}\right]^2 + x^2 \cdot \mathrm{var}(b)$$

Where var(a) and var(b) are respectively the variance of the intercept and the variance of the slope from a Least Square regression analysis.

$$\mathrm{var}(b) = \frac{S_{yy} - (S_{xy}^{\,2}/S_{xx})}{(n-2).S_{xx}}$$

$$\mathrm{var}(a) = \mathrm{var}(b) \cdot \frac{\sum_i x_i^{\,2}}{n}$$

6. Results of the intercomparison programme

Because of the large datasets available (N=3864), it is considered that the general requirements of the Field Test Programme are fulfilled, in terms of the range of concentrations, concentrations of semi-volatile particles, temperature, wind speed etc.

6.1. Uncertainty of the Reference and Candidate Methods

Collocated reference and candidate samplers were not operated during this intercomparison programme, and there are no direct data to determine the "between-instrument" uncertainties. In absence of data available for the Reference Method (KFG), the maximum allowed "between-instrument uncertainty" specified in the Guidance Document has been assumed for use in the calculations, i.e. $U^2_{bs,\,SM} = 1$ µg.m^{-3}

The "between-instrument uncertainty" for the Candidate Method has been based on a comparison carried out by netcen in 1998 (Harmonisation of PM$_{10}$ Monitoring Methods, AEA Technology, April 1998), which operated collocated TEOM 1400 and TEOM 1400 AB analysers for a period of about 2 months. The results of this study are reported in Table 3.

Table 3: "Between-instrument uncertainties" for the Candidate Method for the full dataset and for the dataset corresponding to PM concentrations greater than or equal to the upper assessment threshold specified in DD1 (15 µg.m⁻³).

Database	$U_{bs,\ CM}$	Number of paired data
Full data set	1.03 µg.m⁻³	49
PM_{10} > 15 µg.m⁻³	1.08 µg.m⁻³	43
PM_{10} < 15 µg.m⁻³	insufficient data available	

6.2. Comparison between Candidate and Reference Methods: "Combined Uncertainty" and "Expanded Uncertainty" of the Candidate Method

The results of the comparison are described in Table 4. The slope of the linear relationship between TEOM and KFG data is outside the range 0.9 to 1.1 for each individual site and for the full dataset. A correction factor obtained from the full dataset is applied to all TEOM values ($1/b$ = 1.30 from y = 0.7688x, see Table 4).

Where the linear relationship between corrected TEOM and KFG data has a slope outside the range 0.9 to 1.1, the Candidate Method "fails on slope"; where the "Expanded Uncertainty" W_{CM} is above 25%, the Candidate Method "fails on scatter"; where the slope is inside the range 0.9 to 1.1 and $W_{CM} \leq 25\%$, the Candidate Method is accepted.

After correction using $TEOM_{corr}$ = 1.30.TEOM, the following conclusions may be drawn:

- All sites together: Fails the test based on scatter

- Data > 15 µg.m⁻³: Fails the test based on scatter

- Belfast: Fails the test based on slope

- Glasgow: Fails the test based on slope

- Harwell: Fails the test based on slope

- Marylebone Road: Fails the test based on scatter

- Port Talbot: Fails the test based on scatter

- Thurrock: Fails the test based on slope

6.3. Conclusions

Data collected during the course of an intercomparison programme between collocated TEOM and KFG PM_{10} instruments has been evaluated using the methodology outlined in a draft EC Guidance Document on Equivalence. The expanded uncertainty of the full dataset following correction has been calculated to be 30.5%, and the TEOM therefore fails the test.

The conclusions of this evaluation must however be considered with the following points in mind:

- The reference method (KFG) sampler used in this exercise was fitted with an automatic 8-sample switching option to avoid the requirement for daily site servicing. Whilst this was consistent with the general operation of the network site, there is potential that losses of semi-volatile material may have been occurred from the filters post-sampling, as they remained exposed in ambient conditions for up to 7 days.
- Whilst care in the handling of the filters was taken throughout, there is also the potential for losses of semi-volatile material from the post-sampled filters during the postal transport to the weighing laboratory.
- The between-instrument uncertainty of the KFG has not been determined in this study. Given the potential for losses outlined above, it is not possible to conclude with any certainty whether the stringent criterion defined in the draft Guidance Document was met.

In light of these comments, it is recommended that the Field Test Programme be restructured to bring it fully into line with the requirements of the draft Guidance Document.

An intercomparison exercise according to the draft Guidance Document is planned to start in 2004.

Table 4: Results

Comparison	Linear relationships		R²	Calculation of the uncertainty				
	Raw TEOM data	Corrected TEOM data		$\frac{RSS}{(1+b_2)(n-2)}$	$\left[\frac{a+(b-1)x}{2}\right]^2$	$\mathrm{var}(b){\cdot}x^2$	$u^2_{C-S}(x)$	W_{CM}
All sites together	y = 0.689x + 3.90	y = 0.948x + 3.695	0.67	49.44	0.30	0.09	51.83	29.1%
Data > 15 µg.m⁻³	y = 0.727x + 2.27	y = 1.029x + 0.16	0.56	62.20	0.65	0.18	65.02	32.5%
Belfast	y = 0.593x + 5.61	y = 0.806x + 6.48	0.70	NA	NA	NA	NA	NA
Glasgow	y = 0.573x + 6.28	y = 0.818x + 6.61	0.51	NA	NA	NA	NA	NA
Harwell	y = 0.382x + 7.88	y = 0.537x + 9.57	0.45	NA	NA	NA	NA	NA
Marylebone Road	y = 0.693x + 6.47	y = 0.965 x + 5.80	0.62	55.71	4.101	0.49	62.29	31.8%
Port Talbot	y = 0.758x + 3.68	y = 1.071x + 2.53	0.57	68.41	9.25	0.74	80.39	36.1%
Thurrock	y = 0.539x + 4.47	y = 0.728x + 5.04	0.72	NA	NA	NA	NA	NA

NA: Uncertainty not calculated as the corrected TEOM data fail on slope