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Field test experiments to validate the CEN standard measurement method for PM$_{2,5}$

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Air Quality
Ambient Air

CEN/TC 264/WG 15 PM$_{2,5}$

Field test experiments to validate the CEN standard measurement method for PM$_{2,5}$

Final Report

July 2006

Air Quality

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CEN/TC 264 /WG 15
Standard gravimetric method for the determination of the PM$_{2,5}$ mass fraction of suspended particulate matter

Final Report

Field test experiments to validate the CEN standard measurement method for PM$_{2,5}$

July 2006

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We would also like to thank the numerous unnamed experts dealing with validation measurements and evaluation for their fruitful co-operation.

Secretariat:

Contents

1. Introduction

For air quality across the European Union to be assessed on a consistent basis, Member States need to employ standard measurement techniques and procedures, following Community Directive 96/62/EC on ambient air quality assessment and management [1], and Directive 1999/30/EC (1st EC Air Quality Daughter Directive) [2], which sets the parameters specific to the assessment of particulate matter (and also of sulfur dioxide, nitrogen dioxide and lead).

Prompted by these EU requirements, CEN/TC 264 *Air Quality* established working group CEN/TC 264/WG 15 to present a manual standard gravimetric measurement method for the determination of the $PM_{2.5}$ mass concentration of suspended particulate matter in ambient air.

There are no traceable reference standards for $PM_{2.5}$ measurements. Therefore, the standard measurement method set out in EN 14907 [3] effectively defines the measured quantity by convention, specifically by the sampling inlet design and associated operational parameters covering the whole measurement process.

To support the drafting of the standard measuring method EN 14907, working group CEN/TC 264/WG 15 on $PM_{2.5}$ carried out a field evaluation program at various test locations throughout the EU. Following a pilot study, 8 test locations representative of various ambient air situations were chosen so that the impact of semi volatile particulate matter to the $PM_{2.5}$ mass concentration would be investigated.

The field evaluation was focused on the following aspects:
- to select, validate and assess the practicability of the designated manual gravimetric $PM_{2.5}$ standard measurement method
- to determine the performance characteristics of the standard measurement method, notably measurement uncertainty
- to develop a practical test procedure to demonstrate whether non standard measurement methods (like other manual gravimetric or automatic monitoring methods) are equivalent to the designated standard method.
- to provide information on the performance and measurement uncertainties of some commonly deployed automatic $PM_{2.5}$ measurement methods, in line with the uncertainty requirements set out in the data quality objectives within the Directive 1999/30/EC.

2. Field tests

2.1 Measurement methods

WG 15 agreed that the candidate reference samplers to take part in the Field Test shall comprise:
(1)   the "Mini-WRAC", at the request of the EC;
(2)   a Low Volume "unconditioned" system (with no mechanism to reduce solar heating effects on the sampling line or filter), for comparability with the PM10 standard EN 12341 [4];
(3)   a High Volume system, for comparability with the PM10 standard EN 12341;
(4)   a Low Volume "conditioned" system, with an air flow mechanism designed to reduce solar heating effects, because of the recent understanding of the significance of these effects;
(5)   a US-EPA approved WINS system, for comparability with US-EPA;
(6)   a Sharp Cut Cyclone (SCC) system, because of the potential practical advantages of a cyclone inlet over an impactor inlet, provided that the SCC inlet is not commercially restricted.

The following six sampling systems were chosen as examples for the candidates for the standard method:

- **Mini-WRAC**, a newly developed single filter sampler, with a sample flow rate of approximately 15 m³/h, at the request of the EC, made by the Fraunhofer Institute for Toxicology and Aerosol Research (FhG-ITA), Hannover (Germany).
  The Mini WRAC is a two-stage impactor having cut-off values of 10 µm and 2,5 µm, followed by a back-up filter. The $PM_{2.5}$ fraction is collected on the back-up filter, where the PM_{10} fraction is to be calculated from the sum of the $PM_{2.5}$ fraction and the PM fraction collected on the second stage. For this instrument, the mass flow rate is controlled in terms of moles/sec. This instrument is not equipped with a separate mass flow meter. The mass flow rate is determined according to Bernoulli's law by measuring the pressure drop across to two impactor stages, the ambient pressure and the ambient temperature. To maintain a constant mass flow rate of 0,172 moles/sec (equal to approx. 15 m³/h) the speed of the turbine installed behind the back-up filter is controlled.
  In order to convert the mass flow rate $\dot{v} = 0,172\ \mathrm{moles/sec}$ to the volumetric flow rate given in m³/h the following equation is to be used:

  $$F_a = \dot{v} \cdot R \cdot \frac{T_a}{P_a} \cdot 3.600 \ [m^3/h]$$

  with:
F_a	flow rate related to ambient conditions (T_a, P_a)
R = 8,31 Joule/(mole • K)	gas constant
T_a	ambient temperature in K
P_a	ambient pressure in kP

- **US-EPA approved WINS system**, with a sample flow rate of 1 m³/h, for comparability with US-EPA. Two single filter commercial instruments were used to implement this method during the field experiments:
  o   RAAS 2,5-1, from Thermo Andersen, USA
  o   Partisol FRM Model 2000, from Rupprecht & Patashnick, USA
  The flow rate of the RAAS FRM instrument is measured by means of a temperature-compensated gas meter installed at the outlet of a diaphragm vacuum pump. The volume measured by means of the gas meter per unit of time is automatically converted to ambient conditions by temperature and pressure transducers. To maintain a constant volumetric flow rate the pump's speed is controlled.
  For the Partisol FRM instrument, the mass flow rate is measured by means of a thermal mass flow meter installed between the filter holder and a diaphragm vacuum pump. The mass flow rate is automatically converted to ambient conditions in terms of m³/h by temperature and pressure transducers. To maintain a constant volumetric flow rate a regulating valve installed between mass flow meter and pump is controlled.
  The displayed volumetric flow rate respectively the total air volume sampled over the sampling time was directly used for calculating the $PM_{2.5}$ concentration in terms of µg/m³.

- **Sharp Cut Cyclone (SCC) system**, because of the potential practical advantages of a cyclone inlet over an impactor inlet. This was represented by a Partisol plus Model 2025 with PM_{10} pre-impactor and $PM_{2.5}$ Sharp Cut Cyclone, used as a single filter sampler, with a flow rate of 1 m³/h, from Rupprecht & Patashnick, USA.
  The flow rate control of this instrument corresponds to that one of the Partisol FRM instrument.
  The displayed volumetric flow rate respectively the total air volume sampled over the sampling time was directly used for calculating the $PM_{2.5}$ concentration in terms of µg/m³.

- **Low Volume System**, for comparability with the PM_{10} Standard EN 12341. This was represented by the LVS-3D single filter sampler, with a flow rate of 2,3 m³/h, and an 8-nozzle $PM_{2,5}$ impactor, from Derenda, Berlin (Germany).
  The flow rate of this instrument is measured by means of an orifice plate, not temperature- and pressure-compensated, installed between the filter holder and a rotary vane vacuum pump. On the assumption that the temperature difference between the ambient air and the air in the pump is always constant, the flow rate determined by the orifice plate is corrected by temperature factors for ambient temperatures. Corrections for ambient pressure are made using the ratio of the pressure measured in front of the orifice to the ambient pressure. To maintain a constant flow rate the pump's speed is controlled.
  The displayed volumetric flow rate respectively the total air volume sampled over the sampling time was directly used for calculating the $PM_{2,5}$ concentration in terms of µg/m³.

- **Low Volume System**, similar to EN 12341, but with an air flow mechanism designed to reduce insolation heating effects, because of the recent understanding of the significance of these effects. This was represented by the SEQ 47/50 sampler, with a flow rate of 2,3 m³/h, and an 8-nozzle $PM_{2,5}$ impactor from Leckel Company, Berlin (Germany), used as a single filter sampler.
  The flow rate of this instrument is measured by means of a temperature- and pressure-compensated orifice plate installed between the filter holder and a rotary vane vacuum pump. The flow rate measured by means of the orifice plate is automatically converted to ambient conditions by temperature and pressure transducers. To maintain a constant volumetric flow rate the pump's speed is controlled.
  The displayed volumetric flow rate respectively the total air volume sampled over the sampling time was directly used for calculating the $PM_{2,5}$ concentration in terms of µg/m³.

- **High Volume System**, by analogy with the PM_{10} standard EN 12341. This was represented by the HVS-DHA 80 sampler, with a flow rate of 30 m³/h, and a $PM_{2,5}$ impactor from Digitel, Zurich (Switzerland), used as a single filter sampler.
  The flow rate of this instrument is measured by means of a variable area flow meter installed between the filter holder and a fan blower. This instrument was not equipped with transducers for the ambient temperature and the ambient pressure. Therefore, the flow rate measured by means of the variable area flow meter must be converted to ambient conditions, starting from temperature and pressure values of a nearby meteorological station and the temperature and pressure at the variable area flow meter. To maintain a constant flow rate the blower's speed is controlled.
  The flow rate shown at the scale of the variable area flow meter was converted to the ambient volumetric flow rate by the local operators using the following equation:

$$F_a = F_{FM} \cdot \frac{T_a}{p_a} \cdot \sqrt{\frac{p \cdot p_{cal}}{T \cdot T_{cal}}}$$

with:

F_a	flow rate related to ambient conditions (T_a, p_a) in m³/h
F_{FM}	flow rate shown at the flow meter's scale in m³/h
T_a	ambient temperature in K (average over sampling period)
p_a	ambient pressure in kPa (average over sampling period)
T	temperature in K at the flow meter's entry
p	pressure in kPa at the flow meter's entry
T_{cal}	calibration temperature in K of the flow meter
p_{cal}	calibration pressure in kPa of the flow meter

NOTE on mechanisms to reduce solar heating of sampler inlets:
Theory and experience gained from $PM_{2,5}$ and PM_{10} measurement programmes strongly suggest that there are benefits in designing the sampling system, from the inlet to the filter holder, so as to reduce any heating above ambient temperature especially by strong insolation, as losses of semi-volatile particles are mainly attributed to this effect. Even with design measures in place, some heating losses are expected to occur [5 to 8].

NOTE on flow rate control of candidate standard sampling systems:
It should be pointed out that the flow rate control of the High Volume System is based on STP conditions, whereas
the flow rate control of the other candidate sampling systems is based on ambient conditions of temperature and pressure, in accordance with the provisions of EN 14907.

Following Resolution 51 of WG 15, the following automatic $PM_{2,5}$ instruments were included in the field tests:

- **SM 200 ß-ray attenuation monitor**, sequential filter sampler (1 m³/h flow), with 8-nozzle impactor inlet (OPSIS, Sweden) also equipped with an air flow mechanism to reduce insolation heating effects.
  The flow rate of this instrument is measured by means of a temperature- and pressure-compensated orifice plate installed at the outlet of a diaphragm vacuum pump. The flow rate measured by means of the orifice plate, calibrated with respect to standard conditions (273 K and 101,3 kPa), is automatically converted to ambient conditions by pressure and temperature transducers taking into account the temperature measured at the orifice plate. To maintain a constant volumetric flow rate a regulating valve installed at the pump's entry is controlled.

- **FH62 I-R ß-ray attenuation monitor,** filter tape instrument (1 m³/h flow), with PM_{10} pre-impactor and $PM_{2,5}$ SCC inlet (ESM Andersen Company, Germany).
  The flow rate control of this instrument is in principle the same as for the SEQ 47/50 instrument.

- **BAM 1020 ß-ray attenuation monitor**, filter tape instrument (1 m³/h flow), with 8-nozzle impactor inlet (Met One, USA). Every hour, the filter tape is moved for a new sample (50 min) and dust measurement (10 min).
  The flow rate control of this instrument is in principle the same as for the Partisol FRM instrument.

- **TEOM Tapered Element Oscillating Microbalance** used with the Sample Equilibration System (SES) (1 m³/h flow), 1 m³/h flow with PM_{10} pre-impactor and $PM_{2,5}$ SCC inlet (Rupprecht & Patashnick, USA).
  Behind the inlet the total flow of 1 m³/h = 16,67 l/min is splitted into a major flow of 13,67 l/min and a minor flow of 3 l/min. The minor flow is led by the sampling tube to the filter put on the so-called Tapered Element. The unit consisting of filter and Tapered Element is kept at a constant temperature of 30 °C. The major flow is led directly to the pump.
  The flow rate control of this instrument is in principle the same as for the Partisol FRM instrument.

Other instruments included in the field tests were:

- **8400-N continuous nitrate sampler**, from Rupprecht & Patashnick, USA.

- **manual gravimetric PM_{10} sampler**, following the requirements of EN 12341, provided separately by the operators of each site.

- **meteorological instruments** monitoring temperature, pressure, and relative humidity, provided separately by the operators of each site.

The candidate standard method instruments, the automatic PM$_{2,5}$ instruments, and the nitrate monitor were made available by the manufacturers.

The results in this report are presented anonymously. The candidate standard methods are given random codes CM1 – CM6, while the automatic instruments are given random codes AM1 – AM4.

2.2 Measurement sites

To cover a wide range of relevant ambient air conditions prevailing in Europe the validation tests were performed at a pilot site and eight test sites located in southern, central and northern European countries.

Pilot Site   Berlin (Germany)
General Description   in the city centre adjacent to a very intensive traffic
loaded   city
           motorway
Measurement period   27 September 2000 – 1 February 2001
Weather conditions   Temperature range from approx. -3°C up to 18°C (daily
averages)

           During the measurement period rain and covered sky
      frequently
           occurred.
Pollution situation   The mean PM$_{2,5}$ concentration was approx. 30 µg/m³
           with a maximum value of approx. 90 µg/m³. The nitrate
           concentrations were in the range from approx. 3 µg/m³
           up to 8 µg/m³.

Test sites

Site   Madrid (Spain)
General description   near the crossing of inner city motorways
Measurement period   6 March 2001 – 20 July 2001
Weather conditions   Temperature range from approx. 6°C up to 31°C (daily
averages)

           During the first measurement period up to 20 May fog
           and rain frequently occurred. During the following
           period sunny weather was predominant.
Pollution situation   The mean PM$_{2,5}$ concentration was approx. 13 µg/m³
           with a maximum value of approx. 30 µg/m³. The nitrate
           concentrations were in the range from approx. 0,2
           µg/m³ up to 2 µg/m³.

Site	Vienna (Austria)
General description	at the border of the city centre directly at an intensive traffic loaded city motorway
Measurement period	19 September 2001 – 1 March 2002
Weather conditions (daily averages)	Temperature range from approx. - 11°C up to 20°C
	The weather conditions during the measurement period were typical for a continental autumn and winter with rain, snow, cold and sunny periods.
Pollution situation	The mean $PM_{2,5}$ concentration was approx. 35 µg/m³ with a maximum value of approx. 90 µg/m³. The nitrate concentrations were in the range from approx. 1 µg/m³ up to 10 µg/m³.

Site	Rome (Italy)
General description	near heavy traffic loaded main road in city centre
Measurement period	29 April 2002 – 27 September 2002
Weather conditions averages)	Temperature range from approx. 17°C up to 31°C (daily
Pollution situation	The mean $PM_{2,5}$ concentration was approx. 23 µg/m³ with a maximum value of approx. 40 µg/m³. The nitrate concentrations were in the range from approx. 0 µg/m³ up to 3 µg/m³.

Site	Athens (Greece)
General Description	suburban
Measurement period	30 March 2003 – 24 July 2003
Weather conditions averages)	Temperature range from approx. 7°C up to 29°C (daily
	During the first measurement period rainy weather conditions were prevailing. The following period was frequently dry.
Pollution situation	During the first measuring period there was a pollution episode (pollen) at the site. The mean $PM_{2,5}$ concentration was approx. 24 µg/m³ with a maximum value of approx. 105 µg/m³. The nitrate concentrations could not be measured due to a defect in the nitrate analyser.

Site	Duisburg (Ruhr area, Germany)
General description	suburban with influence from local heavy industry
Measurement period	7 March 2001 – 7 July 2001
Weather conditions (daily averages)	Temperature range from approx. 2,5°C up to 29°C
	During the measurement period relatively cool and sometimes rainy weather conditions were prevailing.
Pollution situation	The mean $PM_{2,5}$ concentration was approx. 21 µg/m³ with a maximum value of approx. 60 µg/m³. The nitrate concentrations were in the range from approx. 0,5 µg/m³ up to 23 µg/m³.

Site	Vredepeel (southeastern part of The Netherlands)
General description	rural situation with high ammonia levels due to intensive pig and poultry farming
Measurement period	6 November 2001 – 15 March 2002
Weather conditions averages)	Temperature range from approx. -3°C up to 11°C (daily

	During the measurement period rain and covered sky frequently occurred.
Pollution situation	The mean $PM_{2,5}$ concentration was approx. 17 µg/m³ with a maximum value of approx. 50 µg/m³. The nitrate concentrations were in the range from approx. 0 µg/m³ up to 6 µg/m³.
Site	Teddington (Greater London, United Kingdom)
General description	suburban
Measurement period	13 January 2003 – 8 May 2003
Weather conditions averages)	Temperature range from approx. 2°C up to 20°C (daily
	During the measurement period relatively cool and sometimes rainy weather conditions were prevailing.
Pollution situation	The mean $PM_{2,5}$ concentration was approx. 22 µg/m³ with a maximum value of approx. 120 µg/m³. The nitrate concentrations were in the range from approx. 0,5 µg/m³ up to 25 µg/m³.
Site	Aspvreten (100 km south of Stockholm, Sweden)
General description	forest situation, close to the Baltic Sea
Measurement period	23 May 2002 – 3 October 2002
Weather conditions averages)	Temperature range from approx. 4°C up to 22°C (daily
	At the beginning and at the end of the measurement period rainy weather periods occurred. During the months August and September dry and sunny weather conditions were prevailing.
Pollution situation	The mean $PM_{2,5}$ concentration was approx. 10 µg/m³ with a maximum value of approx. 45 µg/m³. The nitrate concentrations could not be measured due to a defect in the nitrate analyser.

More details of the monitoring sites are given in Annex A.

2.3   Field test procedures

2.3.1 General overview

- Timing
    - 3 – 6 months per site
    - 2 sites in parallel
      i.e. the first set of instruments was deployed sequentially at the locations Berlin, Madrid, Vienna, Rome and Athens, and the second set of instruments at Duisburg, Vredepeel, Aspvreten and London
    - Q3-2000 until Q3-2003

- Procedures
    - duplicate measurements of candidate standard instruments
    - sampling period: 24 h ± 1 h
    - automatic methods: only single instruments (no duplicate measurements)
    - at least 40, sometimes up to about 100, validated and approved data sets at each site
    - measurements of nitrate concentrations
    - recording of meteorological parameters
      (temperature, pressure, relative humidity, rain, sun)

2.3.2 Operational procedures

Operation procedures covering maintenance, cleaning, and greasing of instruments, the calibration of flow meters, and filter conditioning, storage and weighing, were prescribed in a QA/QC protocol. This is included in this report as Annex B.

3. Data analysis procedures

These procedures are focused on
- Outlier tests on data sets of duplicate candidate standard method measurements
- Intercomparison of candidate standard methods

Outlier tests on data sets from duplicate measurements

The Grubbs outlier test (95 % confidence level) was applied to the duplicate measurements of the candidate standard samplers.

The Grubbs test parameter TP for the data set is given by

$$TP = \left| \frac{D_{extr.} - \langle D \rangle}{s_D} \right| \quad ,$$

where:

$D_{extr.}$ is the maximum difference between any measurement pair, $\langle D \rangle$ the mean and s_D the standard deviation of differences D_i, and where $D_i = | y_{i1} - y_{i2} |$ is the (positive) difference between the measured concentrations (y_{i1}, y_{i2}) of 2 collocated identical samplers.

The test parameter TP was compared with a critical value taken from the standard table, presented graphically in Annex C.

If the value of TP is larger than the critical value given in the table for the appropriate number of pairs, this indicates that the pair having the maximum difference is an outlier, and this pair was removed. The process was repeated until either the critical value was not exceeded, or at most 5% of the data pairs (y_{i1}, y_{i2}) were removed.

No other outlier tests were performed, and no other data removed. For example, no data was removed from the analysis because of differences between different candidate standard methods, or between automatic instruments and candidate standard methods.

Intercomparison of candidate standard methods

For intercomparison purposes, the results of the duplicate measurements of candidate standard methods that survived the outlier test were averaged, to give one daily concentration value for each sampling period of 24 h ± 1 h.

To compare the various candidate standard methods, linear orthogonal regression was used, following Kendall and Stewart [9].

The slope b of the regression line is given by:

$$b = \frac{Syy - Sxx + \sqrt{(Syy - Sxx)^2 + 4.(Sxy)^2}}{2 \cdot Sxy}$$

with:

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

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

$$Sxy = \sum (x_i - \bar{x}) \cdot (y_i - \bar{y})$$

$$\bar{x} = 1/n \sum x_i$$

$$\bar{y} = 1/n \sum y_i$$

The confidence limits of the slope b of the orthogonal regression lines were additionally calculated as follows:

upper and lower bound angles are given by:

$$\arctan b \pm \frac{1}{2} \arcsin \left[2 \cdot t_{95} \sqrt{\frac{Sxx^2 \cdot Syy^2 - Sxy^2}{(n-2) \cdot (Sxx^2 - Syy^2)^2 + 4 \cdot Sxy^2}} \right]$$

where:

t_{95} = Student factor (95% confidence)

The range between the lower and upper bound angles is of course expected to include $\pi/4$ radians. Alternatively the range of the tangents of these angles is expected to include the value 1.

The intercept of the orthogonal regression line with the y-axis, a, is given by

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

4. Data presentation

All data from all of the instruments included in the field tests, both before and after the outliers have been removed, is given in Annex D. The data with outliers removed was used for all analysis procedures.

5. Evaluation of candidate standard methods CM

5.1   Overview of results

In this section, the results for each candidate method are examined individually. The Figures 1 to 6 show scatter plots of the measurements from one instrument against its duplicate instrument, collecting together all available measurements at all sites.

Each of the six figures contains the regression parameters obtained, and also the standard deviation of the differences between duplicate measurements (repeatability), σ_{CM}, calculated from the equation:

$\sigma_{CM}^2 = 1/2n \sum (y_{i,1} - y_{i,2})^2$

16
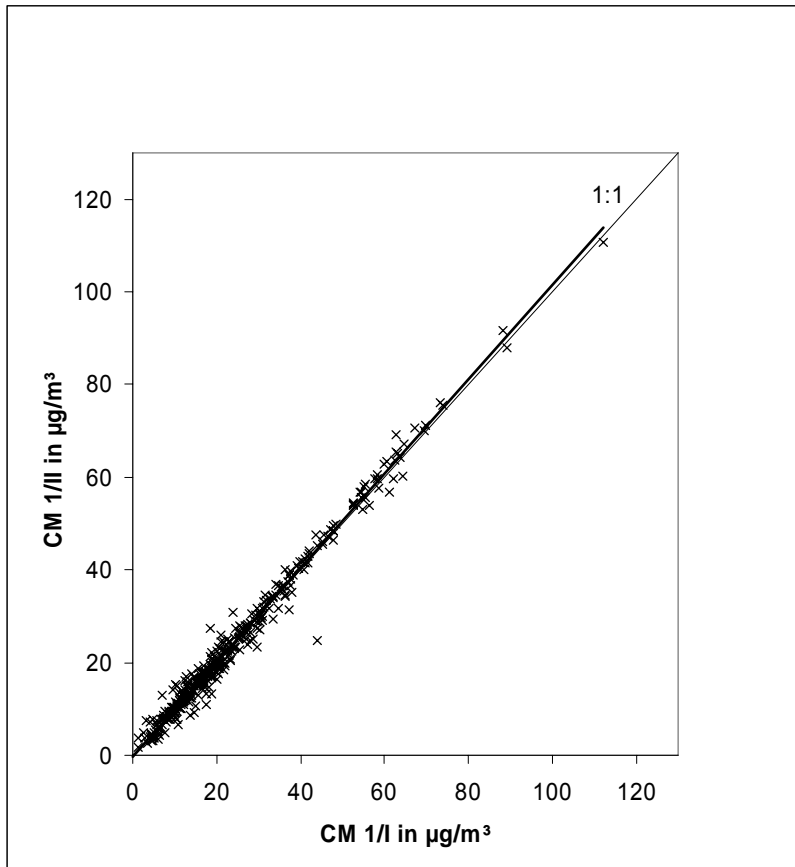
n =	387			
Ortho. regr. y =	- 0,29	+	1,019 x	
S slope =	0,007			
S Intercept =	0,19			
R² =	0,983			
R =	0,992			
AM CM 1/I =	23,69	µg/m³		
AM CM 1/II =	23,84	µg/m³		
AM (CM 1/II / CM 1/I) =	1,02			
S $_{CM\ 1/I}$ =	16,45	µg/m³		
S $_{CM\ 1/II}$ =	16,76	µg/m³		
S$_D$ =	1,54	µg/m³		
S$_{D\ x\ t(95)}$ =	3,04	µg/m³		

Slope 95% confidence limits:
Upper bound = 1,032
Lower bound = 1,005

Figure 1 – CM 1/I vs. CM 1/II for all sites
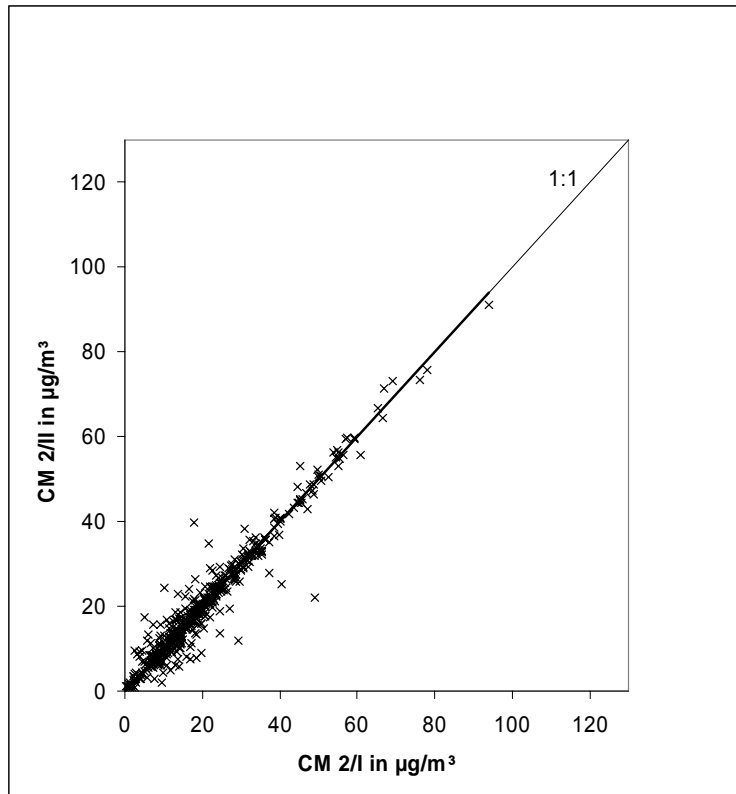
```
                  n =        450
     Ortho. regr.  y =     - 0,14 + 1,004 x
          S slope =       0,011
      S Intercept =        0,29
              R² =        0,942
               R =        0,970
       AM CM 2/I  =      20,88 µg/m³
       AM CM 2/II =      20,11 µg/m³
 AM (CM 2/II / CM 2/I) =     1,03
        S CM 2/I  =      14,45 µg/m³
        S CM 2/II =      14,50 µg/m³
              SD =       2,49 µg/m³
         SD x t(95) =      4,90 µg/m³

Slope 95% confidence limits:
        Upper bound =    1,027
        Lower bound =    0,981
```

Figure 2 – CM 2/I vs. CM 2/II for all sites
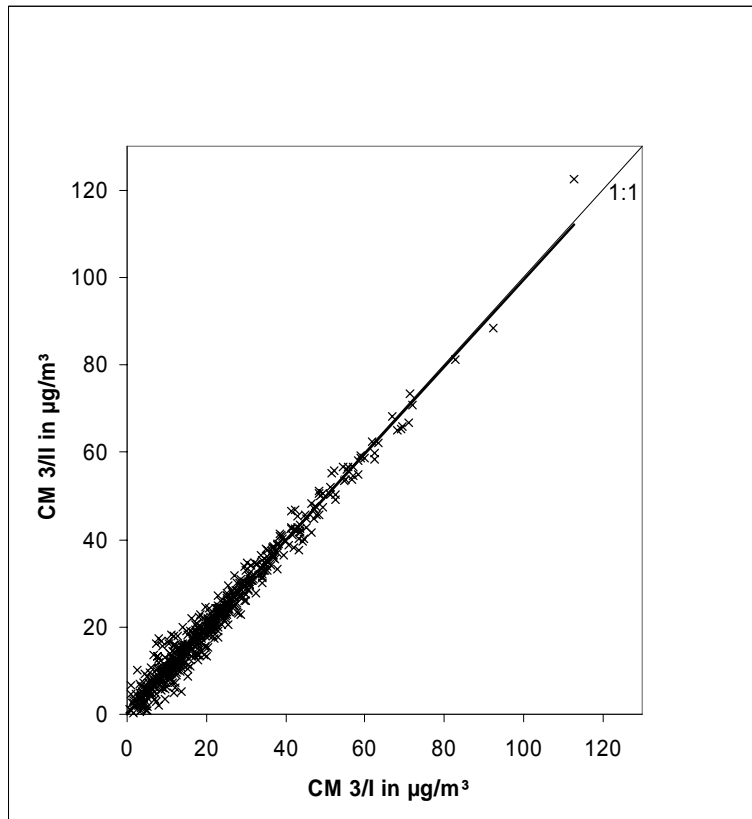
n =	607			
Ortho. regr. y =	- 0,05	+	0,994 x	
S slope =	0,007			
S Intercept =	0,17			
R² =	0,974			
R =	0,987			
AM CM 3/I =	21,43	µg/m³		
AM CM 3/II =	21,24	µg/m³		
AM (CM 3/II / CM 3/I) =	1,03			
$S_{CM\ 3/I}$ =	15,08	µg/m³		
$S_{CM\ 3/II}$ =	14,98	µg/m³		
S_D =	1,73	µg/m³		
$S_{D\ x\ t(95)}$ =	3,39	µg/m³		

Slope 95% confidence limits:

Upper bound =	1,007
Lower bound =	0,981

Figure 3 – CM 3/I vs. CM 3/II for all sites
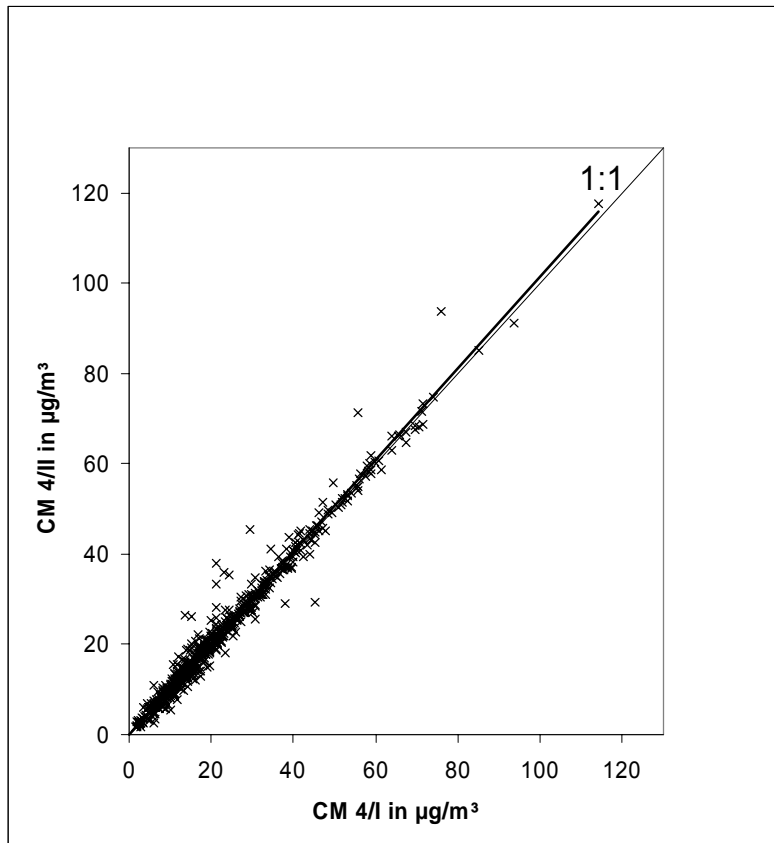
n =	643			
Ortho. regr. y =	- 0,12	+	1,016 x	
S slope =	0,006			
S Intercept =	0,17			
R² =	0,976			
R =	0,988			
AM CM 4/I =	22,44	µg/m³		
AM CM 4/II =	22,69	µg/m³		
AM (CM 4/II / CM 4/I) =	1,02			
$S_{CM\,4/I}$ =	15,45	µg/m³		
$S_{CM\,4/II}$ =	15,70	µg/m³		
S_D =	1,73	µg/m³		
$S_{D\,x\,t(95)}$ =	3,40	µg/m³		

Slope 95% confidence limits:

Upper bound =	1,029
Lower bound =	1,004

Figure 4 – CM 4/I vs. CM 4/II for all sites
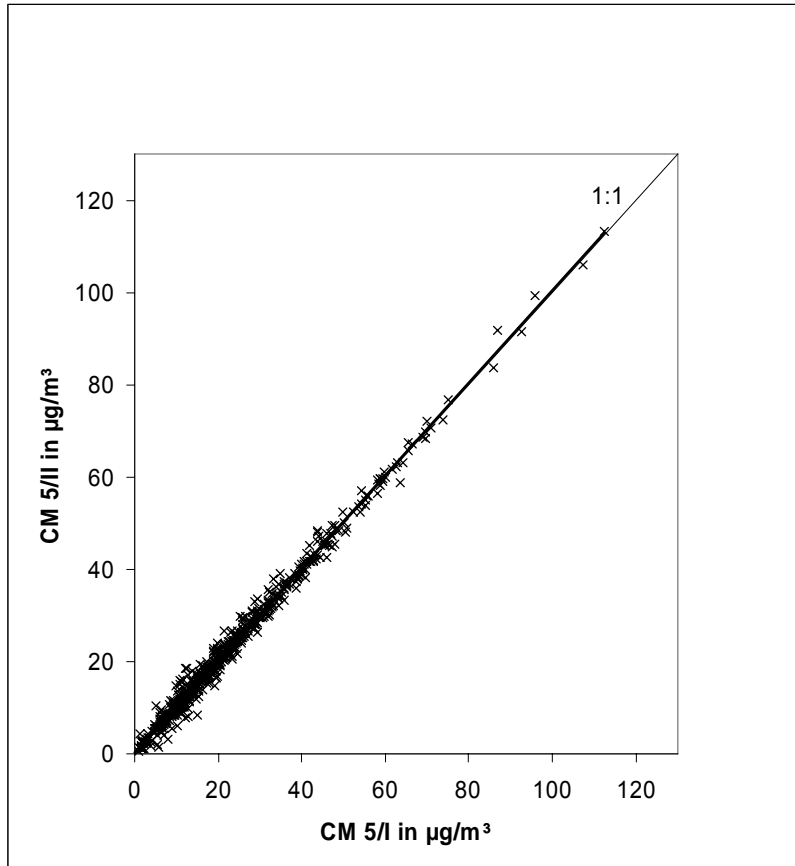
n =	628	
Ortho. regr. y =	0,15 + 1,003 x	
S slope =	0,004	
S Intercept =	0,11	
R² =	0,991	
R =	0,995	
AM CM 5/I =	22,53	µg/m³
AM CM 5/II =	22,76	µg/m³
AM (CM 5/II / CM 5/I) =	1,02	
$S_{CM\ 5/I}$ =	16,38	µg/m³
$S_{CM\ 5/II}$ =	16,43	µg/m³
S_D =	1,14	µg/m³
$S_{D\ x\ t(95)}$ =	2,23	µg/m³

Slope 95% confidence limits:
Upper bound = 1.011
Lower bound = 0.996

Figure 5 – CM 5/I vs. CM 5/II for all sites
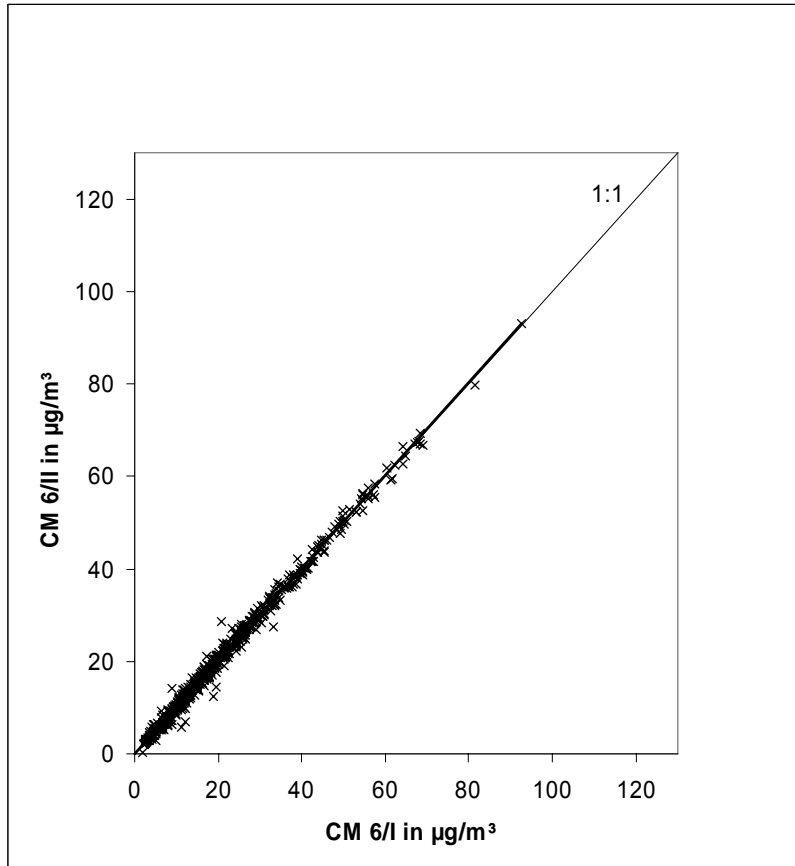
n =	597			
Ortho. regr. y =	0,07	+	1,002 x	
S slope =	0,003			
S Intercept =	0,09			
R² =	0,993			
R =	0,997			
AM CM 6/I =	21,39	µg/m³		
AM CM 6/II =	21,48	µg/m³		
AM (CM 6/II / CM 6/I) =	1,00			
S CM 6/I =	14,63	µg/m³		
S CM 6/II =	14,65	µg/m³		
S_D =	0,86	µg/m³		
$S_{D \times t(95)}$ =	1,69	µg/m³		

Slope 95% confidence limits:

Upper bound =	1,008
Lower bound =	0,995

Figure 6 – CM 6/I vs. CM 6/II for all sites

5.2   Comparison of measured values from different methods

Comparison between methods was done in two ways: firstly a comparison of the concentrations of PM$_{2,5}$ obtained, and secondly a comparison of duplicate repeatability's, as given in the previous section.

Ideally, a valid comparison of concentrations obtained by different methods will use simultaneous measurements that cover the full campaign period at every site. Unfortunately, some of the instruments used in the tests were much less reliable than others, so that the number of measurement days for which concentrations from all six candidate methods are simultaneously available is significantly restricted. The representativeness of the "full simultaneous" data set is therefore limited, but the purpose of identifying if any method gives anomalous results is still served.

In Table 1 all data from all candidate methods is compiled, whereas in Table 2 only those data from all candidate methods is listed that was simultaneously measured at all sites.

Table 1 – Statistical data, all data from all samplers for all sites

Samplers	Number of duplicate meas.	Slope ± std. dev. (orth. regr.)	Slope 95 % confid. limits		Intercept ± std. dev. (orth. regr.)	R²	Mean I / Mean II ± std. dev. µg/m³	Standard deviation of duplicate meas. The SD	Uncertainty duplicate meas. SD x t(95)
			upper bound	lower bound	µg/m³			µg/m³	µg/m³
CM 1	387	1,019 ± 0,007	1,032	1,005	-0,29 ±0,19	0,983	1,008 ± 0,153	1,54	3,04
CM 2	450	1,004 ±0,011	1,027	0,981	-0,14 ±0,29	0,942	1,044 ± 0,344	2,49	4,90
CM 3	607	0,994 ± 0,007	1,007	0,981	-0,05 ±0,17	0,974	1,062 ± 0,459	1,73	3,39
CM 4	643	1,016 ± 0,006	1,029	1,004	-0,12 ±0,17	0,976	1,002 ± 0,149	1,73	3,40
CM 5	628	1,003 ± 0,004	1,011	0,996	0,15 ± 0,11	0,991	1,005 ± 0,199	1,14	2,23
CM 6	597	1,002 ± 0,003	1,008	0,995	0,07 ± 0,09	0,993	1,005 ± 0,194	0,86	1,69

Table 2 – Statistical data, simultaneous data from all samplers for all sites

Samplers	Number of duplicate meas.	Slope ± std. dev. (orth. regr.)	Slope 95 % confid. limits		Intercept ± std. dev. (orth. regr.) µg/m³	R^2	Mean I	Mean II	Standard deviation of duplicate meas. SD µg/m³	Uncertainty duplicate meas. SD x t(95)
			upper bound	lower bound			µg/m³	µg/m³		µg/m³
CM 1	216	1,031 ± 0,009	1,049	1,014	-0,48 ±0,25	0,984	23,27	23,52	1,43	2,82
CM 2	216	0,998 ± 0,018	1,036	0,961	0,02 ± 0,47	0,928	21,41	21,38	2,63	5,19
CM 3	216	0,981 ± 0,011	1,004	0,960	0,26 ± 0,28	0,973	21,05	20,92	1,69	3,33
CM 4	216	0,993 ± 0,007	1,006	0,980	0,11 ± 0,18	0,991	22,76	22,71	1,02	2,01
CM 5	216	0,992 ± 0,007	1,007	0,978	0,60 ± 0,20	0,989	22,69	23,11	1,19	2,35
CM 6	216	0,999 ± 0,005	1,010	0,988	0,29 ± 0,15	0,994	23,65	23,91	0,87	1,71

The WG concluded that no method produced anomalous results, and therefore that no method could be excluded because of expert judgment regarding bias.

6 Selection of standard methods

WG 15 agreed that the standard method would be chosen using the following criteria:

1. expert judgment on the closeness of the measurements to the concentration of the correct component of particulate matter;

2. smallness of the measurement uncertainty of the candidate method. For the purposes of this work, the repeatability of the duplicate measurements was used;

3. reliability and ease of use of the representative instruments during field operation.

Evaluation of the data was therefore aimed at determining whether any methods gave anomalous results, and on the repeatability of the duplicate measurements.

The data with outliers removed was used for this evaluation.

Both CM1 and CM2 were considered to have performed significantly less reliably, judged from their operational problems (number of valid duplicate measurements). The practicability of CM1 was considered as its major drawback. As to CM2, the WG concluded that the standard deviation of duplicate measurements was considerably larger than for the other methods. No further evaluation of these two methods was therefore made, and they were excluded from consideration as a standard method.

Thus, in Table 3 all data from CM 3, CM 4, CM 5 and CM 6 are compiled again for all sites.

Table 3 – Statistical data, simultaneous data from CM 3, CM 4, CM 5 and CM 6 for all sites

Samplers	Number of duplicate meas.	Slope ± standard deviation (orth. regr.)	Slope 95 % confide. limits		Intercept + standard deviation (orth. regr.)	R^2	Mean I	Mean II	Standard deviation duplicate meas. SD	Uncertainty duplicate meas. SD x t(95)
			upper bound	lower bound	µg/m³		µg/m³	µg/m³	µg/m³	µg/m³
CM 3	434	0,994 ± 0,008	1,009	0,979	-0,03 ± 0,20	0,974	20,99	20,84	1,66	3,26
CM 4	434	1,004 ± 0,005	1,015	0,994	-0,08 ± 0,14	0,989	22,41	22,44	1,11	2,18
CM 5	434	0,994 ± 0,005	1,004	0,985	0,43 ± 0,13	0,990	22,51	22,81	1,13	2,22
CM 6	434	1,002 ± 0,004	1,010	0,994	0,13 ± 0,11	0,993	22,21	22,27	0,87	1,70

The WG concluded from this larger set of data that CM3 had a significantly higher duplicate repeatability than the other three methods, and this method was also excluded from further consideration.

Moreover, the WG concluded that the standard method for low volume regimes should be based on the inlet of CM4 and CM5 (which are identical for practical purposes), while the high volume inlet should be based on the CM6 inlet.

Hence, the WG proposes as candidate methods to be used within the standard: CM4/CM5 and CM6, because of their low uncertainties as well as their convenient handling and reliability.

7 Uncertainty

7.1   GUM approach

Following CR 14377, the assessment of measurement uncertainty of the standard measurement method is based on the approach described in the ISO Guide to the expression of uncertainty in measurement (GUM), also published as ENV 13005. The combined standard uncertainty is obtained by adding in quadrature the Type I and Type II uncertainties, where:

- Type I uncertainty is derived from the model equation describing the measurement process, and
- Type II uncertainty cannot be obtained in the same way from the model equation, but has to be taken as the standard deviation of differences between identical samplers in duplicate field tests.

The Type I uncertainty is determined as follows:

- Establishment of a model equation which represents the procedure for obtaining the desired output quantity from the input quantities :

$$C = \frac{m(l) - m(u)}{F \cdot t}$$

The output quantity C is the $PM_{2,5}$ mass concentration; the input quantities are the masses $m(l)$ and $m(u)$ of the loaded and unloaded filter respectively, the flow rate F, and the sampling time t;

- Identification and quantification of all individual sources of uncertainty related to the input quantities, expressed as standard deviations, u_i;

- Combination of the individual uncertainties to obtain a combined type I uncertainty U_I, according to the dependence of the output quantity on the respective input quantity in the model equation. Where the individual sources of uncertainty are independent and all contribute linearly to the output quantity, the combined standard uncertainty u_I is given by:

$$u_I{}^2 = \sum (u_i)^2$$

As to the Type II uncertainty, unlike the situation for most other air pollutants, the lack of representative reference samples means that it is not possible to evaluate the effect of individual sources of uncertainty on the measurement result by systematically varying each one in laboratory tests. However, the combined effect of many sources of uncertainty can be evaluated using field measurements from pairs of collocated samplers simultaneously measuring the same atmosphere, and whose filters are handled in parallel. Specifically, the standard deviation u_{field} of differences between identical samplers ("between sampler uncertainty") serves as a measure of these combined effects of the Type II uncertainty u_{II}, where:

$$u_{II}{}^2 = u_{field}{}^2 = 1/2n \sum (Y_{i,1} - Y_{i,2})^2$$

and $X_{i,1}$ and $X_{i,2}$ are the simultaneous concentration data from the nominally identical samplers 1 and 2.

The combined standard uncertainty follows by adding in quadrature:

$$u^2{}_C = u_I{}^2 + u_{II}{}^2$$

and the expanded uncertainty U by multiplying u_{std} by the coverage factor k:

$$U_{ex,C} = k \cdot u_C$$

The quantity $U_{ex,C}$ is such that there is a 95 % chance that the true value lies within $\pm U_{ex,C}$ of the measured value. Where a sufficient number of degrees of freedom applies, k is taken to be 2.

The expanded uncertainty can then be compared with the Data Quality Objectives (DQO) from Council Directive 1999/30/EC, Annex VIII.

7.2 Uncertainty draft standard measurement methods

The individual sources of the Type I uncertainties for the draft standard measurement methods CM4/CM5 and CM6, the associated Type II uncertainty , and the combined uncertainty are summarised in Tables 4 to 6 (see also EN 14907).

The detailed discussion of the individual type I uncertainties is given in Annex E (see also EN 14907).

Table 4 – Type I uncertainty for CM4/CM5 LVS & CM6 HVS

Contribution	Symbol	CM4/CM 5 Low Volume	CM6 High Volume
Mass m(l) – m(u)	**u_m**		
Inlet performance	u_{mip}	Negligible	Negligible
Transport loss	u_{mtl}	Negligible	Negligible
Filter efficiency	u_{mfe}	Negligible	Negligible
Loss of semi-volatiles	u_{msv}	Zero by convention	Zero by convention
Effect of humidity on filter	u_{mhf}	$40/\sqrt{3}$ μg	$500/\sqrt{3}$ μg
Effect of humidity on particulate	u_{mhp}	$60/\sqrt{3}\ \mu g$	$800/\sqrt{3}\ \mu g$
Buoyancy	u_{mb}	$3/\sqrt{3}\ \mu g$	$30/\sqrt{3}\ \mu g$
Static	u_{ms}	Negligible	Negligible
Contamination	u_{mc}	Negligible	Negligible
Balance : calibration	u_{mba}	$10/\sqrt{3}\ \mu g$	$100/\sqrt{3}\ \mu g$
Balance : zero drift	u_{mzd}	$10/\sqrt{3}\ \mu g$	$100/\sqrt{3}\ \mu g$
Flow	**u_f**		
Calibration	u_c	$3/\sqrt{3}$ %	$3/\sqrt{3}$ %
Drift	u_{fd}	Negligible	Negligible
Time	**u_t**	Negligible	Negligible

Table 5 – Type II uncertainty for CM4/CM5 LVS & CM6 HVS

Contribution	Symbol	Low Volume	High Volume
Field test	**$u_{II} = u_{field}$**	1 μg/m^3	1 μg/m^3

Table 6 – Combined uncertainty for CM4/CM5 LVS & CM6 HVS

Contribution	Symbol	Low Volume	High Volume
Combined uncertainty	**U_c**	1,4 μg/m^3	1,4 μg/m^3

The combined uncertainty is calculated as follows:

Firstly, the combined Type I uncertainty u_l for a given concentration is calculated from the uncertainties for u_m (related to PM$_{2,5}$ mass on the filter) and u_f (related to flow):

$$u_m = \sqrt{\left(\sum u_{mi}^{\;2}\right)}\mu g$$

$$u_f = u_{fc}\%$$

$$u_l = \sqrt{\left(u_m^{\;2}/V^2 + C^2 \cdot u_f^2/100^2\right)}\mu g/m^3$$

where $V = F.t$ is the nominal sampled volume in cubic metres
and C is the mass concentration of PM$_{2,5}$ under consideration, in µg/m^3.

Then, the combined uncertainty for a given concentration is calculated using the following equation:

$$u^2{}_C = u_l{}^2 + u_{field}{}^2$$

The thus determined combined uncertainty amounts to circa 1,4 µg/m^3 for both (LVS and HVS) draft standard methods.

It is worthwhile to note that the combined uncertainty is dominated by the terms u_{mhf} and u_{mhp}, related to filter and inlet tubing conditioning procedures.

7.3 Expanded uncertainty vs. EU Data Quality Objectives

The uncertainties of the draft standard methods CM4/CM5 and CM6 of Section 7.2 are to be compared with the Data Quality Objectives from Directive EU 1999/30/EC, Annex VIII, notably the daily and annual limit values respectively.

For the daily limit value, the expanded uncertainty at a 95 % level of confidence is given by:

$$U_{daily} = 2 \times u_c \ \mu g/m^3$$

The annual value is obtained by averaging 365 daily values, taking into account that components of uncertainty which contribute randomly will have a reduced impact. For the purpose of this standard it is assumed that the u_{field} parameter represents random contributions, while other contributions remain as they were for the daily values.

The annual expanded uncertainty is given by:

$$U_{ann} = 2x\sqrt{\left(U_{field}^{\;2}/365 + U_l^2\right)}\mu g/m^3$$

The following Table 7 summarizes the expanded uncertainty of the standard measurement method (CM) at the daily and annual limit values, together with the EU Data Quality Objectives (DQO).

NOTE At time of preparing EN 14907 no official EU limit values have been established. Therefore, default values have been used, following the provisional suggestions from the CAFE committee. The values given in the table should be considered as indicative, in order to compare with the pertinent DQO's for PM$_{2,5}$, given as percentages.

Table 7 – Expanded uncertainty of the standard measurement method

Default value	EU DQO	LVS CM expanded uncertainty		HVS CM expanded uncertainty	
		$\mu g/m^3$	%	$\mu g/m^3$	%
Daily mean 35 $\mu g/m^3$	25 %	3	9	3	9
Annual mean 20 $\mu g/m^3$	25 %	2	10	2	10

The WG concluded that the expanded uncertainties of both draft standard methods (CM4/CM5 – LVS and CM6 – HVS) are well within the EU Data Quality Objectives, serving the purpose of assessing $PM_{2.5}$ on a consistent basis across the European Union.

8. Comparison of the two standard methods

It is self evident that the two chosen candidate methods CM4/CM5 and CM6 proposed to be used within the standard method should be equivalent.
For practical reasons, CM5 was selected and further used to exemplify the designated standard low volume method.
At the beginning of the measurement period in Athens, there was a severe pollen episode apparently resulting in an unrealistic high scatter of the candidate standard methods. Hence, the WG decided to remove the so called pollen data from the Athens data record. Figure 7 shows the corresponding comparison between the LVS (CM5) and HVS (CM6) candidate standard methods, collecting together all available measurements at all sites, but with the Athens pollen data taken out.
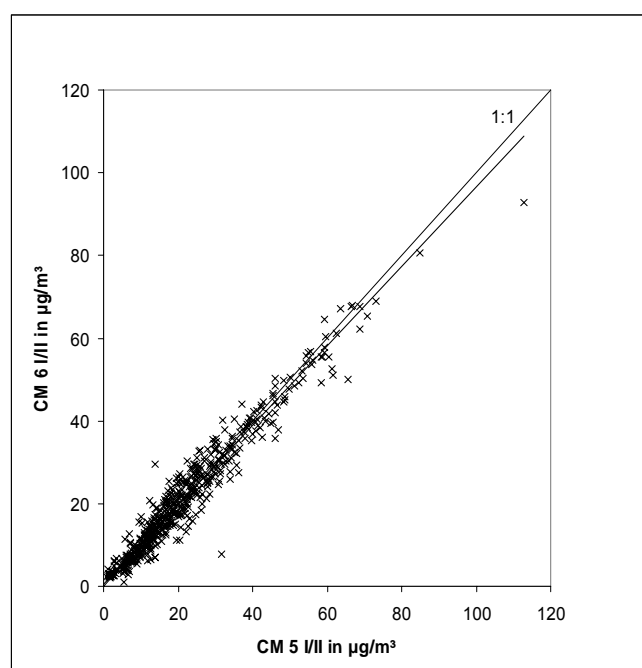
n =	525	
Ortho. regr. y =	0,47 +	0,962 x
S slope =	0,010	
S Intercept =	0,26	
R² =	0,946	
R =	0,973	
AM CM 5 I/II =	21,64	$\mu g/m^3$
AM CM 6 I/II =	21,29	$\mu g/m^3$
AM (CM 6 I/II / CM 5 I/II) =	1,02	
$S_{CM\ 5\ I/II}$ =	15,24	$\mu g/m^3$
$S_{CM\ 6\ I/II}$ =	14,68	$\mu g/m^3$

Figure 7 – CM 6 I/II vs. CM 5 (mean values) (Athens without pollen episode)

So, collecting all data from all sites together suggests a good comparability over all sites between LVS–CM5 and HVS-CM6..

However, upon inspection of the comparability per site the following remarks can be made.

Table 8 – Comparison of HVS vs LVS per site.

		Berlin	Madrid	Vienna
n =		60	71	91,
Ortho. regr. y =		0,974 X - 1,28	1,033 X + 0,17	0,954 X + 2,49
S slope =		0,013	0,062	0,011
S Intercept =	µg/m³	0,41	0,84	0,45
R² =		0,989	0,750	0,987
R =		0,995	0,866	0,994
AM CM5 I/II =	µg/m³	27,89	12,51	34,98
AM CM6 I/II =	µg/m³	25,89	13,1	35,98
AM (CM6 I/II / CM5 I/II) =		0,91	1,09	1,05
$S_{CM5\ I/II}$ =	µg/m³	13,79	5,17	19,12
$S_{CM6\ I/II}$ =	µg/m³	13,44	5,32	18,24
		Rome	Athens	Duisburg
n =		77	31	33
Ortho. regr. y =		1,114 X + 0,00	1,002 X + 1,46	0,836 X + 0,82
S slope =		0,042	0,113	0,032
S Intercept =	µg/m³	0,91	2,51	0,7
R² =		0,898	0,631	0,954
R =		0,948	0,795	0,977
AM CM5 I/II =	µg/m³	20,93	21,31	19,84
AM CM6 I/II =	µg/m³	23,95	22,82	17,41
AM (CM6 I/II / CM5 I/II) =		1,150	1,10	0,89
$S_{CM5\ I/II}$ =	µg/m³	6,270	6,36	8,97
$S_{CM6\ I/II}$ =	µg/m³	7,12	6,37	7,53
		Vredepeel	Aspvreten	Teddington
n =		51	54	56
Ortho. regr. y =		0,881 X - 0,06	0,756 X + 1,28	0,840 X - 0,06
S slope =		0,031	0,021	0,016
S Intercept =	µg/m³	0,6	0,29	0,47
R² =		0,941	0,959	0,981
R =		0,97	0,98	0,99
AM CM5 I/II =	µg/m³	16,8	9,97	20,61
AM CM6 I/II =	µg/m³	14,74	8,82	17,25
AM (CM6 I/II / CM5 I/II) =		0,88	1,15	0,84
$S_{CM5\ I/II}$ =	µg/m³	9,76	9,63	21,03
$S_{CM6\ I/II}$ =	µg/m³	8,63	7,32	17,7

It is seen from Table 8 that the regression slopes range between 0,76 and 1,11. Specifically, the two HVS-CM6 devices successively used at the sites in Duisburg, Vredepeel, Aspvreten and Teddington showed negative deviations from the two LVS-CM4/5 devices by roughly 12 % up to 25 % (i.e. roughly up till some 3 µg/m³). At the same time, the two LVS-CM5 devices gave generally similar measurements to the other samplers such as CM2, CM3 and CM4 at these sites.
The two HVS-CM6 devices that were employed in the sequence Berlin, Madrid, Vienna, Rome and Athens gave comparable results to the two LVS-CM5 devices with the exception of Rome.

At the Rome site the HVS-CM6 devices showed higher measurements than the LVS-CM5 devices by approx. 11 % (again some 3 μg/m^3). Again, the LVS-CM5 devices gave similar results to CM2, CM3 and CM4.

In Annex F some possible reasons for the differences are discussed..

9. Equivalence procedure

The issue of determining whether a non-standard method gives results equivalent for regulatory purposes to a standard method is relevant to many air pollutants as well as PM$_{2,5}$. Since these field tests were planned, an ad-hoc EC working group has been established to address equivalence for all pollutants in a comprehensive and uniform way.
Pending the development of an appropriate equivalency procedure, the WG carried out the aforementioned comparison (Section 8) of the two (LVS and HVS) standard methods to assess their "comparability", as part of the WG draft report finalized in December 2004.

In the meantime, the recommended EU equivalency procedure was developed by the ad-hoc EC working group, and officially adopted by the EU CAFE Steering Committee at its April 2005 meeting.
In Annex G equivalence is judged using the aforementioned „officially" recommended EU equivalency procedure.

The equivalence procedure given as Annex A of EN 14907 is closely based on the discussion draft version of the equivalence working group document. The field tests were not directly used to establish this procedure.

It should be emphasized that CEN/TC 264/WG 15 does not have the authority to declare any of the non-standard methods used in the field tests (manual or automatic) equivalent. Nor was it the aim of the field tests to produce definitive data from which equivalence could be determined. The data will be relevant, but any decision will depend on the details of the final standard method and the detailed requirements of the final equivalence testing procedure.

10. Presentation of automatic PM$_{2,5}$ instrument results

The data for the four automatic instruments included in the field tests, described in Section 2.1, is given in Annex D. It is the purpose of this report to provide this data for further evaluation elsewhere, rather than to form any conclusions about the automatic instruments.

As a preliminary summary of the results, the data is presented here in the following ways.

Firstly, for each automatic instrument, given a random label AM1, AM2, AM3 or AM4, each available day's data for one selected site (close to a motorway and dominated by traffic) is plotted against the same day's data from one of the standard methods (CM5) as a scatter plot. The site has been chosen to show relatively good agreement between the automatic instrument and the standard method. Secondly, similar scatter plots are presented for all measurements at all sites together. In both cases, linear orthogonal regression parameters were calculated, using the procedures of Section 3. No outlier tests were used and no data removed.

Figures 8 to 11 show the data from the aforementioned sites. In these cases a good correlation is observed, with a value of R^2 of 0,94 or higher, indicating that with suitable correction algorithms, in these conditions, good agreement between various automatic instruments and the standard method can be obtained.
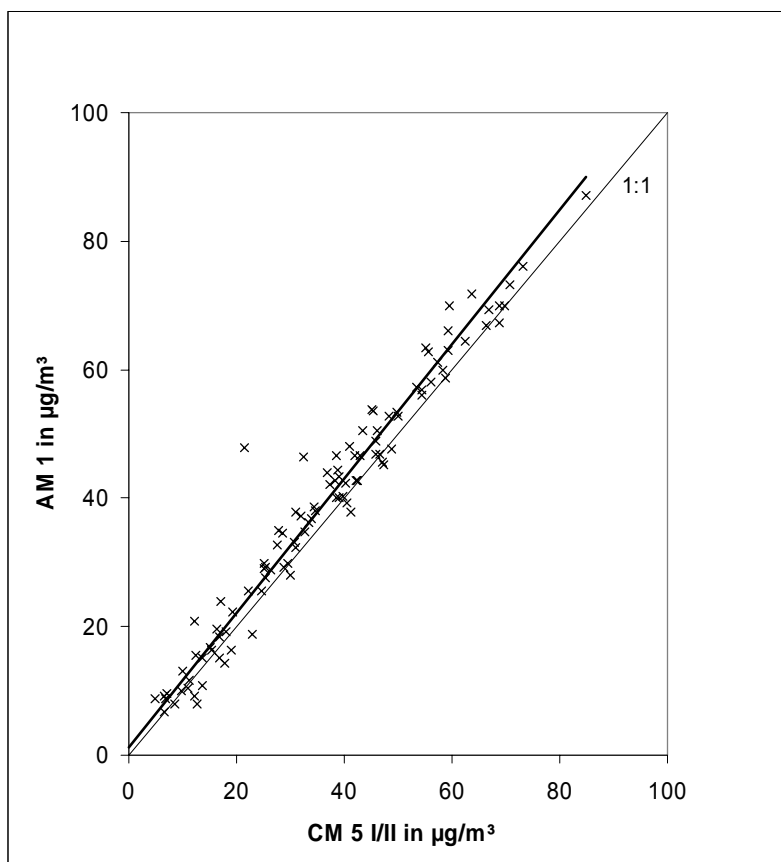
n =	103	paired values	
Ortho. regr. y =	1,26	+ 1.045 x	
S slope =	0,022		
S Intercept =	0,87		
R² =	0,957		
R =	0,978		
AM CM 5 I/II =	36,04	µg/m³	
AM AM 1 =	38,91	µg/m³	
AM (AM 1 / CM 5 I/II) =	1,10		
S CM 5 I/II =	18,53	µg/m³	
S AM 1 =	19,35	µg/m³	

Figure 8 – CM 5 I/II vs. AM 1
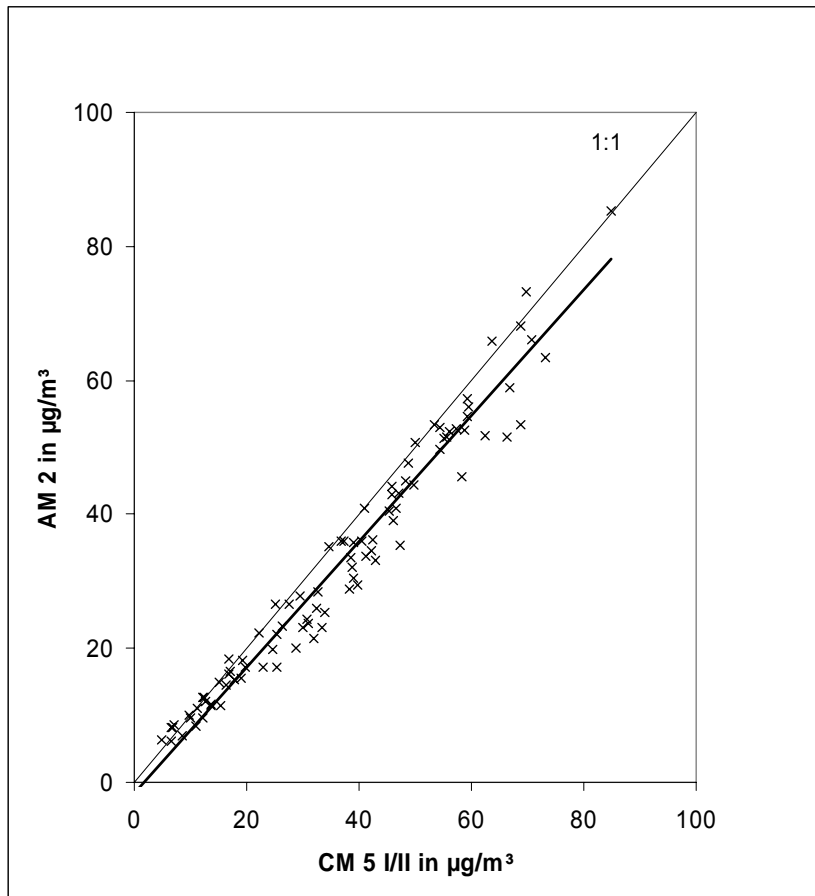
n =		92	paired values
Ortho. regr. y =		- 1,60	+0,938 x
S slope =		0,020	
S Intercept =		0,83	
R² =		0,959	
R =		0,979	
AM CM 5 I/II =		36,26	µg/m³
AM AM 2 =		32,42	µg/m³
AM (AM 2 / CM 5 I/II) =		0,90	
S CM 5 I/II =		19,41	µg/m³
S AM 2 =		18,24	µg/m³

Figure 9 – CM 5 I/II vs. AM 2
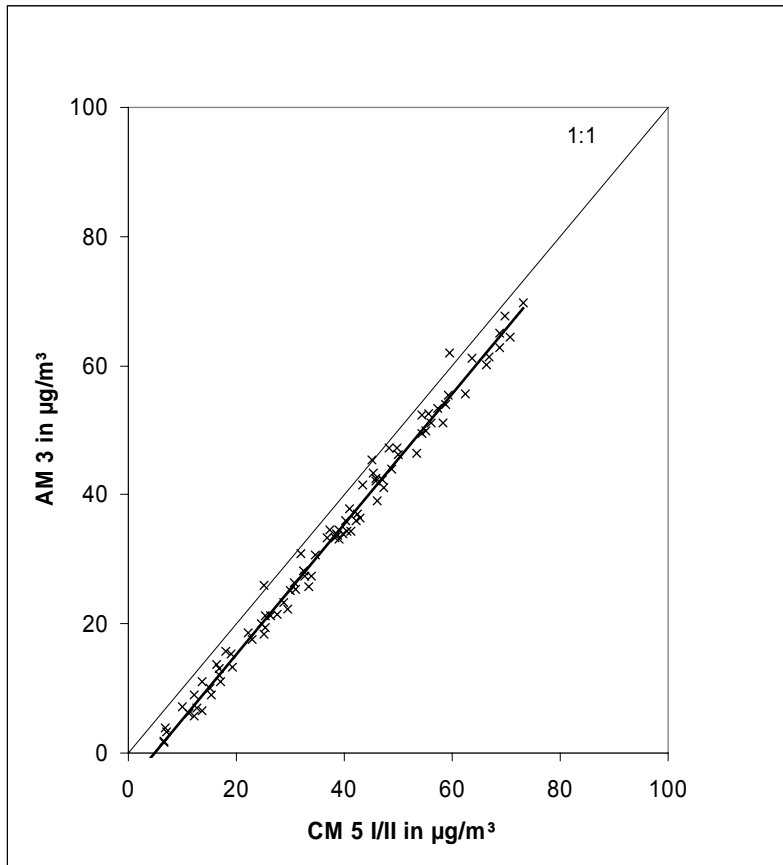
	n =	87	paired values
Ortho. regr.	y =	- 4,91	+1,011 x
S slope =		0,011	
S Intercept =		0,46	
R² =		0,989	
R =		0,995	
AM CM 5 I/II =		37,16	µg/m³
AM AM 3 =		32,67	µg/m³
AM (AM 3 / CM 5 I/II) =		0,83	
S $_{CM 5 I/II}$ =		17,90	µg/m³
S $_{AM 3}$ =		18,10	µg/m³

Figure 10 – CM 5 I/II vs. AM 3
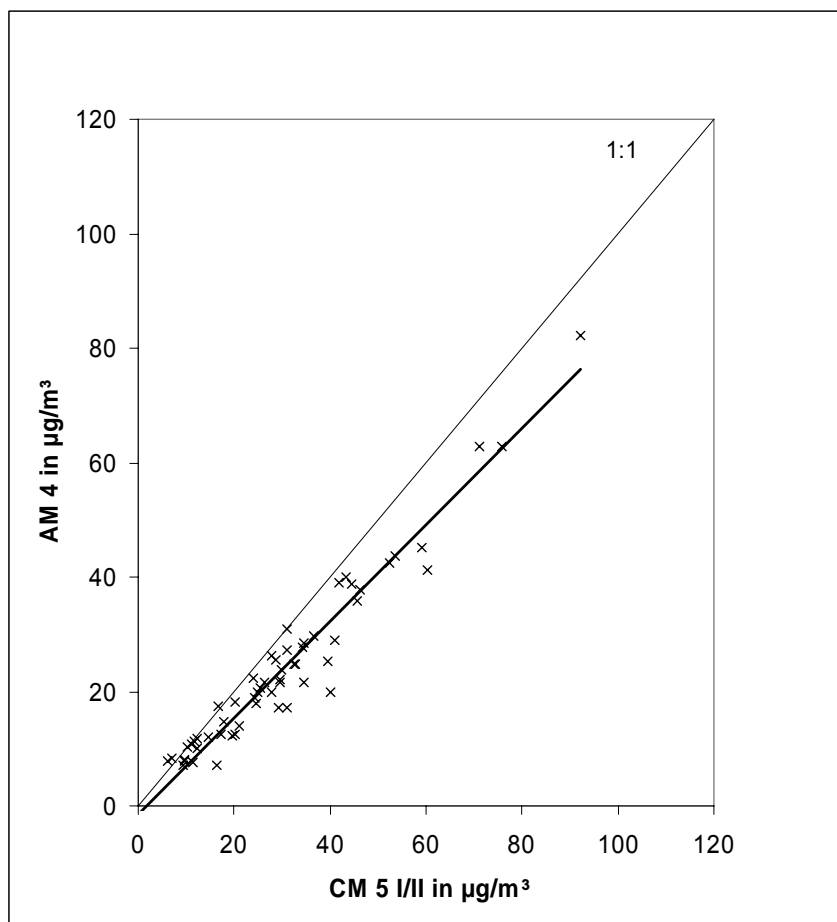
n =	57	paired values
Ortho. regr. y =	- 1,51	+0,846 x
S slope =	0,028	
S Intercept =	1,00	
R² =	0,939	
R =	0,969	
AM CM 5 I/II =	30,38	µg/m³
AM AM 4 =	24,18	µg/m³
AM (AM 4 / CM 5 I/II) =	0,81	
S $_{CM 5 I/II}$ =	17,83	µg/m³
S $_{AM 4}$ =	15,15	µg/m³

Figure 11 – CM 5 I/II vs. AM 4

Next, Figures 12 to 15 show the data for each automatic instrument for all sites combined. In all cases the scatter of the data is significantly worse than in the previous examples, indicating that the agreement between the automatic instruments and the standard methods varies at different sites and in different conditions. This is to be expected in view of the way semi-volatile material is treated in the various automatic instruments, and provides support for the requirement within the equivalence procedure for candidate instruments to pass several independent comparability tests. Moreover, these examples show that equivalence does not necessarily cover in a uniform way the wide range of prevailing conditions within the European Union. Equivalence could also be limited to specific ambient situations at national or regional level within EU member states.
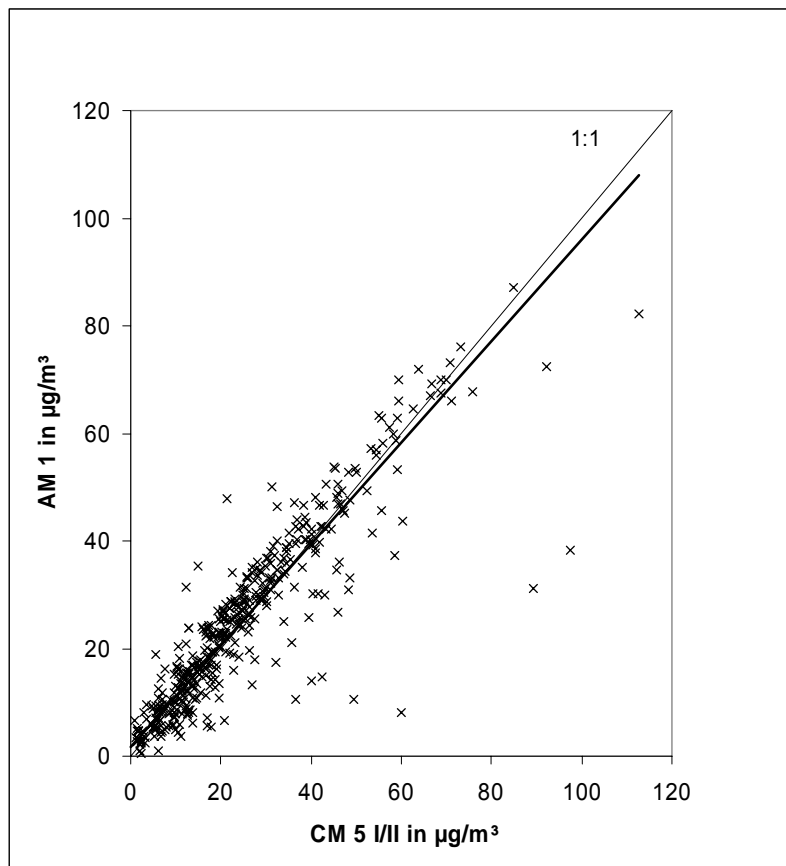
	n =	426	paired values
Ortho. regr. y =		1,83	+0,942 x
S slope =	0,021		
S Intercept =	0,63		
R^2 =	0,795		
R =	0,892		
AM CM 5 I/II =	24,62	µg/m³	
AM AM 1 =	24,03	µg/m³	
AM (AM 1 / CM 5 I/II) =	1,12		
$S_{CM\ 5\ I/II}$ =	17,55	µg/m³	
$S_{AM\ 1}$ =	16,65	µg/m³	

Figure 12 – CM 5 I/II vs. AM 1 for all sites
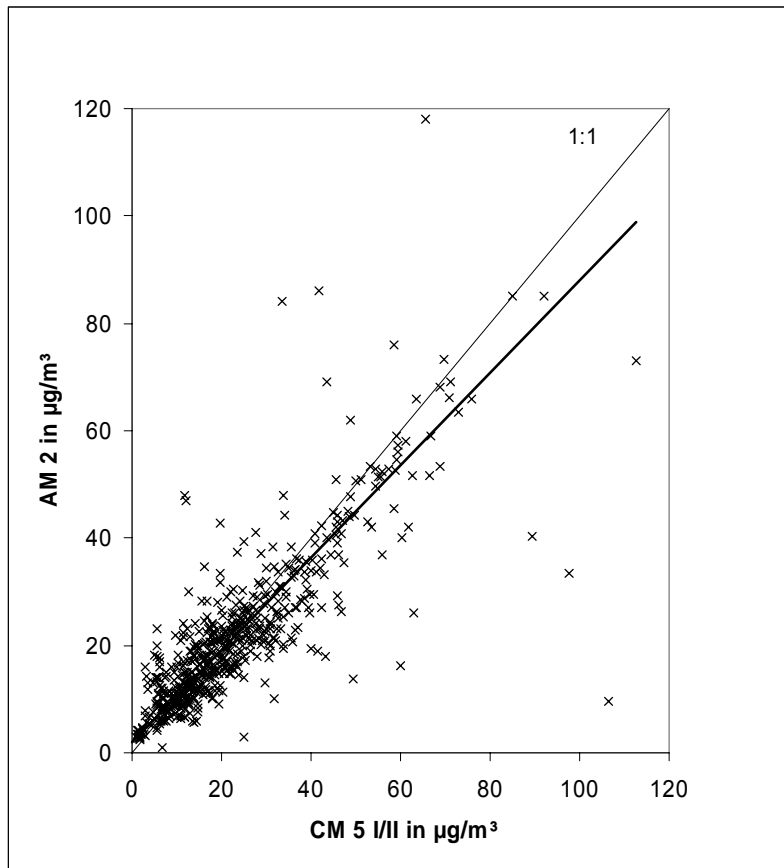
n =	585	paired values
Ortho. regr. y =	2,00	+0,858 x
S slope =	0,021	
S Intercept =	0,60	
R² =	0,660	
R =	0,812	
AM CM 5 I/II =	22,95	µg/m³
AM AM 2 =	21,70	µg/m³
AM (AM 2 / CM 5 I/II) =	1,10	
S CM 5 I/II =	16,63	µg/m³
S AM 2 =	14,68	µg/m³

Figure 13 – CM 5 I/II vs. AM 2 for all sites
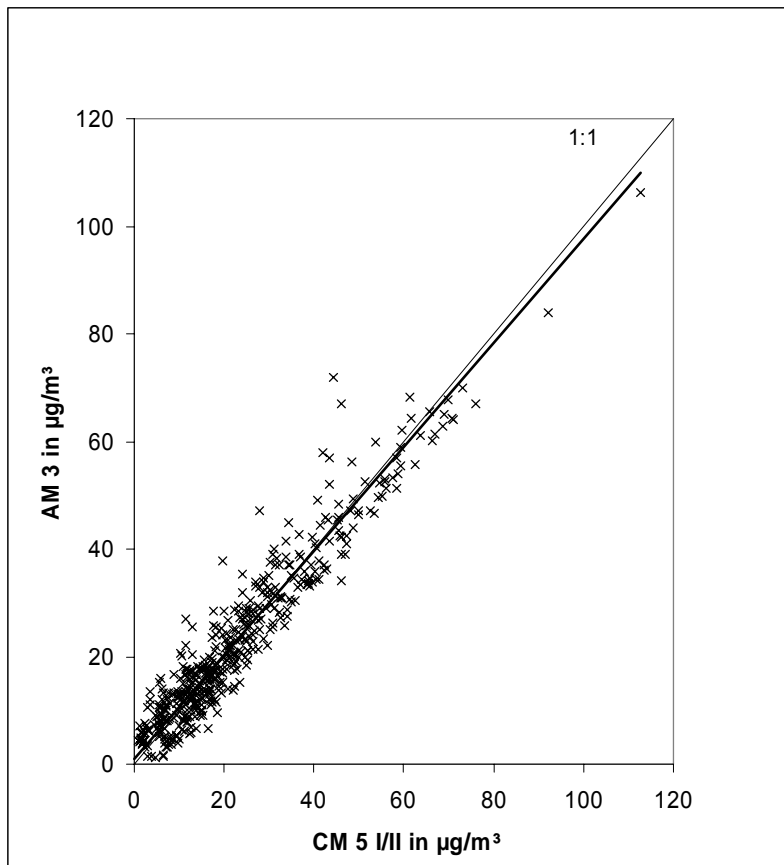
	n =	460	paired values
Ortho. regr.	y =	1,01	+0,967 x
S slope =		0,014	
S Intercept =		0,38	
R² =		0,909	
R =		0,953	
AM CM 5 I/II =		22,75	µg/m³
AM AM 3 =		23,01	µg/m³
AM (AM 3 / CM 5 I/II) =		1,15	
S CM 5 I/II =		16,50	µg/m³
S AM 3 =		15,99	µg/m³

Figure 14 – CM 5 I/II vs. AM 3 for all sites
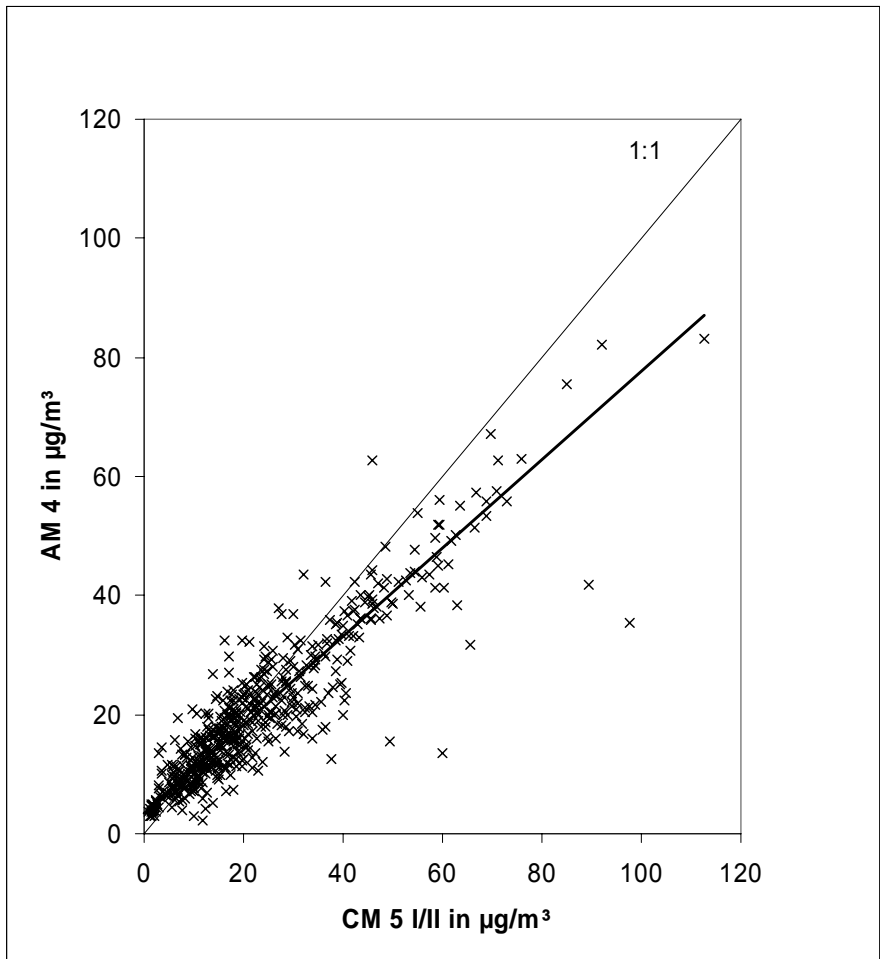
	n =	538	paired values
Ortho. regr.	y =	3,56	+0,742 x
	S slope =	0,014	
	S Intercept =	0,40	
	R² =	0,813	
	R =	0,902	
	AM CM 5 I/II =	22,88	µg/m³
	AM AM 4 =	20,53	µg/m³
AM (AM 4 / CM 5 I/II) =		1,06	
	S CM 5 I/II =	16,76	µg/m³
	S AM 4 =	12,79	µg/m³

Figure 15 – CM 5 I/II vs. AM 4 for all sites

11. PM$_{2,5}$ vs. PM$_{10}$

In order to investigate the relation between PM$_{10}$ fraction, measured according to the EN reference method, and the PM$_{2,5}$ fraction, PM$_{10}$ concentrations were also measured at eight sites. The data is given in Annex D. Mainly PM$_{10}$ low volume reference samplers conforming to EN 12341 were used, but other manual PM$_{10}$ samplers and automatic PM$_{10}$ instruments, calibrated by PM$_{10}$ low volume reference samplers, were also used. In Table 9 the mean PM$_{2,5}$ and PM$_{10}$ concentrations and their ratios are compiled. For this evaluation, a small number of data pairs showing higher PM$_{2,5}$ than PM$_{10}$ concentrations were eliminated. The mean ratio PM$_{2,5}$ to PM$_{10}$ is 0,65 with a standard deviation of 0,15. The correlations PM$_{2,5}$ vs. PM$_{10}$ gave variation coefficients (R²) in the range of approximately 0,7 up to 0,95.
It should be pointed out that these results are representative only for the specific sites during the measurement periods upon consideration, and can not necessarily be considered as yearly averages.

Table 9 – Ratio PM$_{2,5}$/PM$_{10}$

Site	No. of values	PM$_{2,5}$ (CM 5) µg/m³	PM$_{10}$ µg/m³	PM$_{2,5}$/ PM$_{10}$
Berlin	42	23,6	30,9	0,74
Vienna	103	35,8	49,2	0,70
Rome	79	20,9	38,0	0,55
Athens	42	24,2	39,0	0,63
Duisburg	41	19,5	30,3	0,63
Vredepeel	62	18,6	31,5	0,58
Aspvreten	40	8,0	9,9	0,78
Teddington	56	22,8	32,9	0,62
Mean (from single data pairs)			35,4	0,65
Standard deviation			19,7	0,15

12. Conclusions

The two proposed EN 14907 standard methods CM4/CM5-LVS and CM 6-HVS are characterized by their convenient handling and operational reliability. Besides, their low uncertainties are well within the EU data quality objectives, serving the purpose of assessing PM$_{2,5}$ on a consistent basis across the European Union.

However, the HVS implementation of the standard method did give lower results than the CM4/CM5 LVS device.

As to equivalence, it should be emphasized that CEN/TC 264/WG 15 does not have the authority to declare any of the non-standard methods used in the field tests (manual or automatic) equivalent. Nor was it the aim of the field tests to produce definitive data from which equivalence could be determined.

As to the automatic instruments, at individual specific sites a good correlation is observed, with a value of R^2 of 0,94 or higher. This finding indicates that with suitable correction algorithms, in these specific site conditions, good agreement between various automatic instruments and the standard method can be obtained. However,

when comparing the automatic instruments with the standard one for all sites combined, the scatter of the data is significantly worse than per site separately. This is indicating that the agreement between the automatic instruments and the standard methods varies at different sites and in different conditions. This is to be expected in view of the way semi-volatile material is treated in the various automatic instruments, and provides support for the requirement within the equivalence procedure for candidate instruments to pass several independent comparability tests.

Moreover, this also shows that equivalence does not necessarily cover in a uniform way the wide range of prevailing conditions within the European Union. Equivalence could also be limited to specific ambient situations at national or regional level within EU member states.

Annex A

Detailed information about the sampling locations

Berlin (Germany)

The measurements were carried out after the new set-up of the instruments at the measuring site at the city motorway in Berlin during the period from 27th September 2000 up to 1st February 2001.

The site in Berlin is located next to a crowded city motorway (geographical co-ordinates: 52,5°N, 13.3°E). The traffic volume at this part of the highway is about 150.000 cars per 24 hours with a proportion of trucks of 10 to 15 %. The samplers were installed on a container station. The site is surrounded by the city highway in the east, residential houses in the west and northwest and a cemetery in the south. Besides the traffic emissions, the site is affected by all sorts of emissions from the city such as from house heatings, small trades etc. and resuspended material.

Figure A.1 – Berlin monitoring site

Madrid (Spain)

The sampling point is situated in a populated residential area of Madrid (Spain). The city located in the centre of the Iberian Peninsula (40° 25' N; 03° 43'W at 660 m above sea level) has around 4 millions of inhabitants. Madrid has a high vehicle density, underwent daily traffic jams. The sampler and analysers (set on two designated containers) as well as the meteorological station were situated in an open plateau near to main northwest street networks. The minimum distance to the closest building has been of 100 meters.

Figure A.2 – Madrid monitoring site

Vienna (Austria)
The measurement period in Vienna was 19 September 2001 to 1 March 2002. The sampling site was at the border of the city centre directly at an intensive traffic loaded city motorway)

The weather conditions during the measurement period were typical for a continental autumn and winter with rain, snow, cold and sunny periods. The temperature range was from approx. - 11°C up to 20°C (daily averages)

Figure A.3 – Vienna monitoring site

Rome (Italy)

The Environmental Hygiene Laboratory (EHL) at the Italian National Institute of Health (ISS) is located in an area with various public buildings (hospitals, university and other public or private office buildings. The city centre is located 1,5-2,0 kilometers west from the site. The monitoring station itself is located on the premises at EHL next to a large street with a traffic volume of some 25.000 cars / day. The ratio of diesel to gasoline light-duty vehicles in the area is approximately 1:10. The area is not subject to any direct industrial emission. The heating season lasts 5 months (Nov-March). For residential heating mainly gas and oil are used. This site can be described as traffic-oriented.

Temperature during the two semesters April-October and November-March ranges between 13-32 °C and 5-24 °C respectively. Wind velocity at the site is quite constant and about 0.3-0.5 m/s with one hour maxima from 1,6 to 3,6 m/s. Relative humidity, based on 24h average, is variable between 40% and 80%.

Figure A.4 – Rome monitoring site

Athens (Greece)

The measurement campaign took place between 30th March and 31 July 2003 at the Environmental Research Laboratory at N.C.S.R. "Demokritos" in Aghia Paraskevi, in Athens. Aghia Paraskevi is approximately 12 km to the northeast of central Athens and is a semi-urban area. The site is situated on the foot on Mountain Hemittos and it covers an area of 600 acres in a nice forest of pine trees. Close to the monitoring site the Hemettous mountain peripheral road was under construction during the Athens campaign.

Figure A.5 – Athens monitoring site

Duisburg (Germany)
The location of the measurement station is in the centre of Duisburg, and can be described as an urban background station. It is placed on the campus of the university Duisburg-Essen at Bismarckstraße (easting/northing: 2,554,557/5,699,573). The distance to the next minor street is about 80 m and to the next building 15 m. The outdoor samplers were all located on a 2m high platform and automatic samplers in a climatized container . Main industries are steel industry approximately 2-5 km in the northwest and southwest of the sampling station, and a major harbour in the west-northwest direction. Several major motorways surround the city area at a distance of 2-5 km in all directions.

Figure A.6 – Duisburg monitoring site

Vredepeel (The Netherlands)

The test site is located in a rural surrounding. During some seasons the volatile compounds such as ammonium nitrate will be increased, due to the permission of the manure transport. The measured mean particle nitrate concentration during the field test was 1 µg/m^{-3}, due to the winter season.

Figure A.7 – Vredepeel monitoring site

Teddington (UK)

The measurement campaign took place between 13th January and 9th May 2003 at the National Physical Laboratory in Teddington, Middlesex. Teddington is approximately 30km to the south west of central London and is in an urban area. The site was located on the edge of a Royal Park and is classified as an urban background site.

Figure A.8 – Teddington monitoring site

Aspvreten (Sweden)

The campaign lasted from end of May until beginning of October 2002 at the field station Aspvreten. Aspvreten is situated about 68 km south east of Stockholm City in an area of fields, mixed forests and lakes., and some 2 km from the Baltic Sea. The main local sources for particles are Studsvik (3 km; combustion research plant), Oxelösund (23 km; ironworks with blast furnace) and Nyköping (23 km; combustion plant).

For the measuring campaign, two containers placed side by side were used. On top of the first container a platform for the gravimetric reference instruments was built. On the roof of the second container the inlets for the automatic instruments were installed and connected through the roof to the automatic instruments kept inside the container.

Figure A.9 – Aspvreten monitoring site

Annex B

QA/QC procedures

B.1 Sampling and weighing procedure

This section covers the Quality Assurance and Quality Control measures which were used in the field study.

B.1.1 Weighing room procedures

Weighing room conditions shall be monitored and documented.
The following procedures shall be applied at every weighing session.
Filters shall always be handled with tweezers (stainless steel or PTFE-coated).
All filters shall be visually checked prior to use for defects such as holes or loose material, and discarded if defects are found.
At the beginning of each weighing session the proper functioning of the balance shall be checked with reference weights with similar mass to the filters, as a measure of accuracy and drift of the balance. If the reading of the balance differs by more than 10 µg for LVS or 100 µg for HVS from the reference weight, the situation shall be investigated and resolved before proceeding.
A static discharger shall be used on PTFE filters prior to weighing.

NOTE 1   A static discharger is not necessary with glass fibre or quartz filters.

Two blank reference filters of the same size and material as those used for the measurement shall be kept in the weighing room. Their weight shall be recorded at each weighing session, as a measure of climatic conditions affecting the weight of the LVS and HVS filters.
For the LVS design, if the masses of the blank reference filters have changed by less than 30 µg since the last weighing session, their average mass shall be recorded, and weighing of LVS filters can proceed. If the masses of the blank reference filters have changed by more than 30 µg, the situation shall be investigated and resolved before proceeding.
For the HVS design, if the masses of the blank reference filters have changed by less than 390 µg since the last weighing session, their average mass shall be recorded, and weighing of HVS filters can proceed. If the masses of the blank reference filters have changed by more than 390 µg, the situation shall be investigated and resolved before proceeding.

NOTE 2   The aforementioned changes in mass of 30 µg and 390 µg for LVS and HVS blank reference filters respectively are equivalent to a change in measured concentration of about 0.55 µg/m³ (at nominal flow and 24 h of sampling).

B.1.2 Unloaded filter weighing

Unloaded filters shall be conditioned in the weighing room for a minimum of 48 h before weighing.

NOTE 1   Conditioning of PTFE filters takes place within a few minutes. Conditioning for 48 h is required nevertheless.

Filters shall be weighed twice, with an interval of at least 12 h, to confirm that the filter weight has stabilised. If the weights differ by a mass more than 55 µg for LVS or 720 µg for HVS, the particular filter shall be discarded.

The unloaded filter mass shall be taken as the average of the two separate measurements.
Unloaded filters may be stored in the weighing room for up to 10 days before sampling.

B.2 Sampling

The sampling period shall be 24 h ± 1 h, and shall be recorded with an accuracy of ± 5 min.

B.2.1 Sample storage and transport procedures

All loaded and unloaded filters shall be left unfolded and protected during storage and transport, for example in the filter holder, in clean glass petri dishes, or similar containers.
Within 4 h of the end of the sampling period, loaded filters shall be returned to the weighing room or be placed within a storage / transport facility. Loaded filters may be kept within the storage / transport facility for a period of up to 15 days before being placed in the weighing room.

B.2.2 Loaded filter weighing

Loaded filters shall be weighed at least 48 hours after being placed in the weighing room, and then again after a further 24 h – 48 h. If the weights differ by a mass more than 55 µg for LVS or 720 µg for HVS the result shall be noted but not recorded as valid data.

NOTE   The aforementioned differences in mass of 55 µg for LVS and 720 µg for HVS are equivalent to a difference in measured concentration of 1 µg/m³ (at nominal flow and 24 hours of sampling).

The loaded filter mass shall be taken as the average of the two separate measurements.

B.3 Additional quality assurance and quality control

This section covers quality assurance and quality control activities additional to those in Clause 6, to be used on a less frequent basis.

B.3.1 Maintenance of the sampling system

Maintenance of mechanical parts of the sampling system shall be carried out according to the manufacturer's instructions.
Sample inlets shall be cleaned and greased according to the manufacturer's requirements, taking into account local particulate concentrations. If no instructions on cleaning intervals are given by the manufacturers the inlets shall be cleaned and greased at least as frequently as every 15th sample.

B.3.2 Calibration

B.3.2.1 Flow rate

The flow rate for the reference LVS and HVS instruments shall be checked against an appropriate transfer standard flow meter traceable to a national or international standard, at least every three months or every 20th sample. The expanded

uncertainty (at 95 % confidence) of the transfer standard flow meter measurements shall be better than 2 % at laboratory conditions.

If the flow rate determined using the transfer standard deviates more than 2 % from the value required for correct operation of the inlet, the flow controller shall be adjusted according to the manufacturer's instructions.

B.3.2.2 Ambient temperature and pressure sensors

Where temperature and pressure measurements separate from the flow control unit are needed to produce the correct $PM_{2,5}$ concentration (i.e. with ambient volume units), ambient temperature and pressure shall be determined using adequately calibrated instrument.

B.3.2.3 Balance

The balance shall be calibrated against appropriate weights traceable to national or international standards at least once a year.

B.3.2.4 Weighing room temperature and relative humidity sensors

The uncertainty (95 %) of the temperature measurement shall be better than ± 0,5 °C, and of the relative humidity measurements better than 2,0 % RH.
The sensors shall be checked against appropriate transfer standards every 3 months, and calibrated against appropriate traceable national or international standards at least once a year.

B.3.2.5 Field blanks

Blank filters which are conditioned alongside filters used for sampling shall be weighed before and after transportation to the monitoring site together with the filters used for sampling. The detailed procedure for use of these field blanks to assess local factors affecting filter weighing is left to the local operator. If the blank weights differ by a mass more than 55 µg for LVS or 720 µg for HVS the reason shall be investigated.

NOTE   The aforementioned differences in mass of 55 µg for LVS and 720 µg for HVS are equivalent to a difference in measured concentration of 1 µg/m³ (at nominal flow and 24 h of sampling).

Annex C

Grubbs critical values
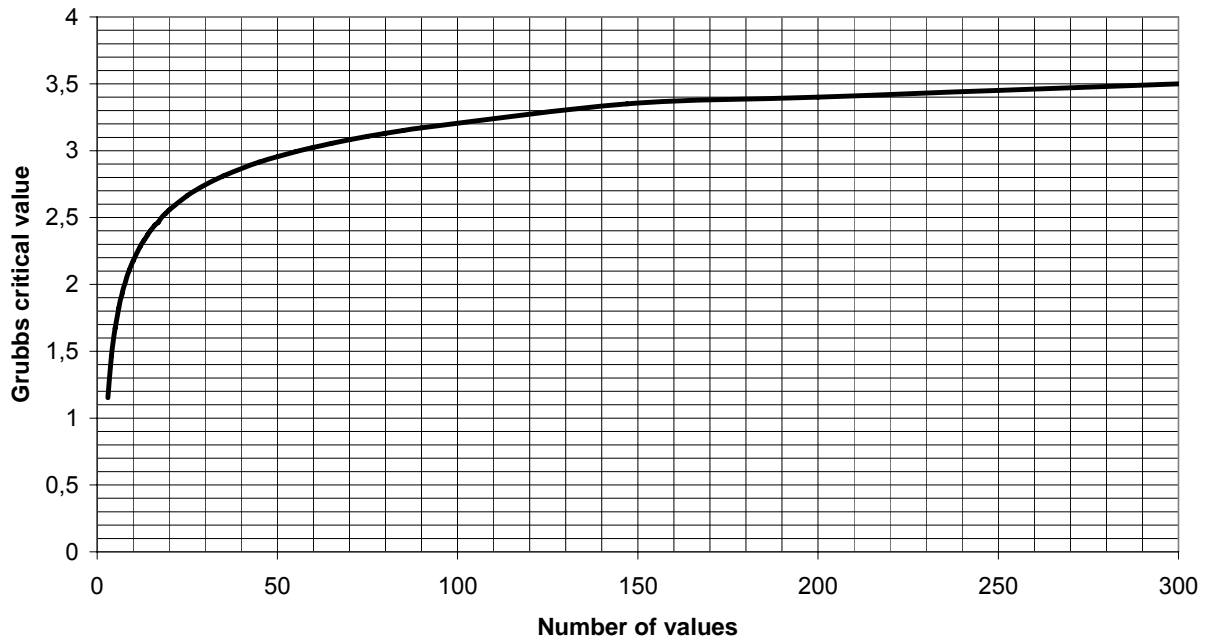
Figure C.1 – Grubbs critical values (95 % confidence level; see Clause 3)

Annex D

All field test data without and with outliers.

D.1 All field test data without outliers

The data can be downloaded at.
 http://ies.jrc.cec.eu.int/fileadmin/H04/Air_Quality/data_without_outliers.xls

D.2 All field test data with outliers

The data can be downloaded at
http://ies.jrc.cec.eu.int/fileadmin/H04/Air_Quality/data_including_outliers.xls

Annex E

Individual sources of type I uncertainty

E.1 General

This section covers the individual sources of Type I uncertainty following Clauses 9.2.1 to 9.2.3 from EN 14907.

The individual sources of Type I uncertainties for the draft standard measurement methods CM 5-LVS and CM 6-HVS can be deducted from the model equation describing the procedure for obtaining the desired output quantity: $PM_{2,5}$ concentration C from the input quantities: collected particulate mass, flow rate and time.

$$C = \frac{m(l) - m(u)}{F \cdot t}$$

where:
- C is the concentration, in µg/m³
- $m(l)$ is the loaded filter mass, in µg
- $m(u)$ is the unloaded filter mass, in µg
- F is the volume flow rate at ambient air conditions, in m³/h
- t is the sampling time, in h

Individual uncertainty sources within each of these input measurements are given below:

E.2   Collected particulate mass *m(l) – m(u)*

E.2.1   Change of mass because inlet particulate size selection performance deviates from the designated characteristic

The designated particulate size selection characteristic for the $PM_{2,5}$ fraction of suspended particulate matter is defined in Clause 5.1.1 of EN 14907 (standard inlet design), when used at the correct flow rate. Deviations in transmitted size fraction will therefore depend on:

— deviations from the ideal mechanical design due to dimensional tolerances, build up of dust, or inadequate greasing;

— deviations from the designated flow rate.

These deviations are limited by the design tolerances in Clause 5.1.1 (standard inlet design) and the procedures set out in Clauses 6 (sampling and weighing procedures) and 7 (quality assurance and control) of EN 14907, and can be considered as negligible.
Also, deviations in transmitted size fraction will depend on the ambient temperature, because of the temperature dependence of the viscosity of the ambient air. The $PM_{2,5}$ cut-off diameter changes by about 1,5 % for a temperature change of 10 K. Since very little of the mass in the $PM_{2,5}$ fraction is found in particles close in size to the cut-off diameter, the effect on the sampled mass is considered to be negligible.
It is considered that any random contribution to the measurement uncertainty will be incorporated within the field test parameter u_{field}.

E.2.2 Deposition losses in the connecting pipework

There are several different mechanisms which can potentially lead to losses of particulate matter in the pipework between the inlet and the filter. Turbulent inertial deposition is the most critical mechanism, but for $PM_{2,5}$ the loss within tubing up to 3 m length is expected to be less than 0,1 %.

Losses due to gravitational settling and inertial deposition are made negligible by using vertical sampling lines, and avoiding flow constrictions (such as bends) in the sampling line. Losses due to electrostatic deposition are made negligible by using electrically conducting pipework.

Other factors influencing the transport losses in the connecting pipework are thermophoretic and diffusiophoretic deposition, which are kept negligible by avoiding a large temperature drop between the connecting pipework and the sampled air. These factors are all limited by the requirements in Clause 5 of EN14907, describing the standard sampling system.

Finally, particle diffusion is only significant for very small particles, which have a negligible contribution to the observed $PM_{2,5}$ mass.

It is considered that any contribution to the measurement uncertainty will be negligible.

E.3   Filter collection efficiency

Losses of particulate matter due to transmission through the filter are expected to be very small, and are limited by the requirement on filters in Clause 5 (standard sampling system) of EN14907.

It is considered that any contribution to the measurement uncertainty will be negligible.

E.4   Loss of semi-volatile particulate matter between collection and weighing

It is known that substantial fractions of $PM_{2,5}$ mass can be composed of semi-volatile components, such as ammonium nitrate, which can volatilise at any time between entry to the sampling inlet and weighing of the loaded filter, at a rate predominantly determined by the temperature of the sampling system and the filter.

This volatilisation loss is limited within the reference measurement method by the constraints on the sampling system components set out in Clause 5.1 (sampling systems components), and on sample storage, transport and conditioning set out in Clauses 5 and 6 (sampling system, and sampling and weighing procedures respectively) of EN 14907.

Hence, some loss of semi-volatile material is expected when this standard is followed. However, the definition of $PM_{2,5}$ for the purpose of this standard incorporates these losses of semi-volatile material. Therefore, the average effect of volatilisation losses on the measurement of $PM_{2,5}$ is considered to be zero by convention, when the constraints set out in EN 14907 are followed.

The effect on uncertainty of variation in losses of material from similar samples experiencing similar storage, transport and conditioning will be included in the variation within the field test, u_{field}.

Variations in loss of semi-volatile material due to variations in sample storage, transport and conditioning permitted within the constraints set out within Clause 6 (sampling and weighing procedures) of EN 14907 will not have been evaluated within the field tests, and are assessed separately.

E.5　Change in filter mass between the unloaded and loaded weighings (excluding the particulate mass) due to water content

It is known that the mass of filters, without any collected particulate matter, varies with humidity in a way which varies between filter materials, and also between filters of nominally the same material.

For the purpose of this standard only changes in the effect of humidity between the unloaded and loaded weighings are relevant. This effect is controlled by the conditioning requirements for unloaded and loaded filters set out in Clause 6 (sampling and weighing procedures) of EN14907.

The contribution to measurement uncertainty due to variations of humidity on the filter will be partially included in the variation determined within the field test, u_{field}. However, a change in average relative humidity from say 46 % to 54 % between the unloaded and loaded filter weighing sessions would be permissible according to EN 14907 the standard but will not have been accounted for in the u_{field} parameter, as the individual filters will have experienced the same conditions. The maximum effect is quantified by the constraints on mass change on unloaded filters at separate weighing sessions given in Clauses 6.1 and 6.2 (weighing procedures and unloaded filter weighing) of EN 14907.

E.6　Variation in mass of particulate matter due to water content

A second function of the conditioning constraints is to bring the collected particulate matter to a standard level of water content by prescribing the temperature and relative humidity before and during weighing.

The effect of this on the uncertainty of the measurement is quantified by the constraint on mass change at the separate weighings of loaded filters given in Clause 6.5 (loaded filter weighing) of EN 14907.

E.7　Changes in buoyancy effects between the unloaded and loaded weighings

The density of the surrounding air, which causes a buoyancy effect on the weight of the filters, is predominantly determined by the air pressure and temperature. Of these only the temperature is controlled as part of Clause 6 (sampling and weighing procedures) of EN 14907. The effects of changing conditions between weighing sessions would not be assessed by the field tests.

However, the expected effects of buoyancy changes can be calculated from physical principles to be less than 3 µg for LVS filters, and less than 30 µg for CM 6 HVS filters.

E.8　Balance accuracy and zero drift

Typical balances have a repeatability and accuracy, when calibrated, of less than 10 µg for CM 5 LVS filters and 100 µg for CM 6 HVS filters (see Clause 5.2 on weighing facilities of EN 14907). This is clearly negligible in comparison with the mass changes covered in Clauses 9.2.1.5 and 9.2.1.6 of EN 14907 (regarding change in filter mass between the unloaded and loaded weighings, due to water content, and variation in mass of particulate matter due to water content respectively).

Uncorrected zero drift of a well calibrated balance can lead to errors of 10s of µg for CM 5 LVS filters and 100s of µg for CM 6 HVS filters. These errors are controlled by the procedures for use of reference weights set out in Clause 6 of EN 14907 (sampling and weighing procedure).

The contribution to uncertainty will be determined by the criteria in Clause 6 (sampling and weighing procedure) of EN 14907.

E.9   Effects of static electrical forces during weighing

Static electrical charge is known to have a potentially significant effect on the weighing of PTFE filters. However, the correct use of a static discharger as required in Clause 6 of EN 14907 is considered to control this. Any effect is considered to be included in the variation determined within the field test, u_{field}.

E.10   Contamination or loss of filter material between unloaded and loaded weighings

It is possible to introduce significant errors in the weight of collected particulate matter because of the loss of filter or particulate material during handling and transport, or the addition of matter not collected during sampling. The procedures for handling, storage and transport in Clause 6 of (sampling and weighing procedure) are designed to control these factors. The contribution to the uncertainty in normal use of EN 14907 is considered to be included in the variation determined within the field test, u_{field}.

E.11   Flow (F)

The flow measurement can be based on several different physical principles, which have different influencing factors. However, the uncertainty is controlled by the requirements on the flow system set out in Clause 5.1 (sampling system components) of EN 14907 the parameters needing to be controlled shall be established by the operator in each case.

There will be two components of the flow uncertainty, firstly arising from the accuracy of the transfer standard used for calibration, and secondly from any net deviation from the required flow rate from the calibrated value over the period of the measurement. As set out in Clause 5.1 (sampling system components), the average flow is controlled to within ± 2%, while the flow meter is calibrated against a transfer standard with an uncertainty of less than 2 %. These figures have been combined in quadrature to give an effective contribution in Table 4, for the uncertainty contribution to flow not covered by the field tests, of 3 %.

Flow measurement can also be influenced by differences in flow rate between the sampling head and the flow meter, pressure drop over the filter, wind, temperature and pressure influences on the flow meter, and leakage in pipework or around the filter holder. These factors are controlled by the QA/QC procedures in Clause 7 of EN 14907 (additional quality assurance and control), and any residual contribution to the uncertainty is considered to be included in the variation determined within the field test, u_{field}.

E.12   Time (t)

There are two elements which may contribute to the uncertainty of the time measurement.

Firstly, the timing device may be running fast or slow. With any modern timing device this will be a negligible effect for the purpose of this standard.

Secondly, there will be some difference between the measured time and the actual time during which the filter was sampling at the required flow rate. Following Clause 6.3 (sampling period) of EN 14907, the maximum difference is required to be 5 min over the sampling period of 24 h, a variation of 0,35 %. Again, any effect on the uncertainty is considered to be negligible.

E.13   Field test uncertainty

The uncertainties u_{field} used in EN 14907 were obtained from the field study undertaken by CEN/TC 264/WG 15 on $PM_{2,5}$, carried out over almost 3 years at 9 sites such that a broad range of relevant ambient parameters prevailing within European countries was covered.

The uncertainties u_{field} were derived from the results from all the sites using the equation given in 9.1 of EN 14907.

Annex F

Comparison between the designated LVS and HVS standard measurement methods

Regarding the observed differences between the HVS/CM6 and LVS-CM4/5 , the WG explored whether deviations from operational procedures and/or technical design features of the HVS-CM6 device could be identified as possible reasons.

As to the *operational procedures* only one possible deviation could be identified. Two different calibration flow meters were used to perform the flow calibration of the HVS-CM6 devices successively used at the sites in Duisburg, Vredepeel, Aspvreten and Teddington, respectively Berlin, Vienna, Madrid, Rome and Athens.) Differences between these different calibration flow meters could result in systematic differences between the employed flow settings of the HVS-CM6 devices on site. In its turn this could give rise to a systematic difference in total flow between the aforementioned two measurement trails, hence systematic differences between the corresponding HVS-CM6 devices.

However, after a thorough examination of the results of the comparisons between HVS-CM6 and CM4/5 for the two sample trails, WG 15 concluded that the differences observed could not be attributed to a systematic difference between the two flow calibration devices.

As to technical design features, the possibility of deviating impactor diameter has been considered. A (slightly) deviating diameter would result in a (slightly) deviating cut off diameter, giving rise to a systematic positive or negative deviation of the HVS-CM6 results from the LVS-CM4/5 one's. As pointed out before, both negative and positive deviations have observed. Hence, this possibility has also been ruled out as highly improbable.

Another technical design feature considered was termed by the WG the "Reynolds number" option.
Considering the Reynolds number Re of the flow in the impactor jets of the HVS and LVS sampling inlets reveals the following:

$$Re = V D (\rho / \eta) = 4 Q / (\pi D v)$$

With
V = velocity in impactor jet
D = inner diameter of impactor jet
Q = flow rate in impactor jet
ρ = air density   = $1{,}2 \times 10^{-3}$ g/cm^3
η = absolute viscosity   = 181 micropoise = 181×10^{-6} cm^{-1} g s^{-1}
$v = \eta / \rho$ = kinematic viscosity   = $0{,}15$ cm^2 s^{-1}

The following Table summarizes the Re numbers for the LVS and HVS impactors

Table F.1 – Re numbers for the LVS and HVS impactors

	LVS	HVS
D	2,6 mm = 0,26 cm	5,6 mm = 0,56 cm
Q	2,3 m^3/h	30 m^3/h
# of impactors	8	10
Q per impactor	$\{2{,}3 \times 10^6 / 3600\}/8$ = 80 cm^3/s	$\{30 \times 10^6 / 3600\}/10$ = 833 cm^3/s
Re	2607	12631

For LVS the Reynolds number Re ≈ 2600, and for HVS ≈ 12600, implying a laminar flow regime in the LVS impactor jets, and a turbulent one for HVS. If it is assumed that both impactors work on the basis of a laminar flow design, this difference may explain the difference in sampler behaviour. However, the pertinent effects are hard to judge. It is recommended to further explore this option starting from an appropriate experimental study (either in the laboratory or in the field).

Annex G

Equivalence of PM standard measurement methods according to EU equivalency procedure

In Section 8, the HVS and LVS PM$_{2,5}$ standard methods were directly compared to each other. It was concluded that HVS and LVS PM$_{2,5}$ did compare realistically well over all sites together
But it was also concluded that there are real site dependent differences between LVS–CM5 and HVS-CM6.

The above mentioned preliminary assessment of Section 8 was part of the WG draft report finalized in December 2004.
In this Annex, equivalence is judged using the „officially" recommended EU equivalency procedure adopted by the EU CAFE Steering Committee at its April 2005 meeting; see also Annex A of EN 14907.
This concerns:
- Equivalence of the two LVS PM$_{2,5}$ standard methods CM4 and CM5.
- Secondly, the equivalence of HVS vs. LVS is considered once again.

Equivalence LVS-CM4 vs. LVS-CM5
The next tables show the results of the equivalence procedure, collecting together all available measurements at all sites, and per site separately.
When data from all sites are combined, the equivalence criteria are fulfilled.
Only for the Athens site the equivalence criteria are not fulfilled. However, based on the observed between-sampler uncertainty of 4,8 μg/m^3 the results from the Athens site are not acceptable for equivalence testing *a priori*.

Table G.1 – Equivalence procedure for LVS-CM4 vs. LVS-CM5 with all available measurements at all sites

		All sites	
REGRESSION OUTPUT			
slope b		1,001	
uncertainty of b		0,005	
intercept a		-0,25	
uncertainty of a		0,14	
number of data pairs		576	
EQUIVALENCE TEST			
random term	μg/m^3	1,62	
bias at LV	μg/m^3	-0,21	
combined uncertainty	μg/m^3	1,64	
relative uncertainty		4,7%	Pass
ref between-sampler u	μg/m^3	1,16	

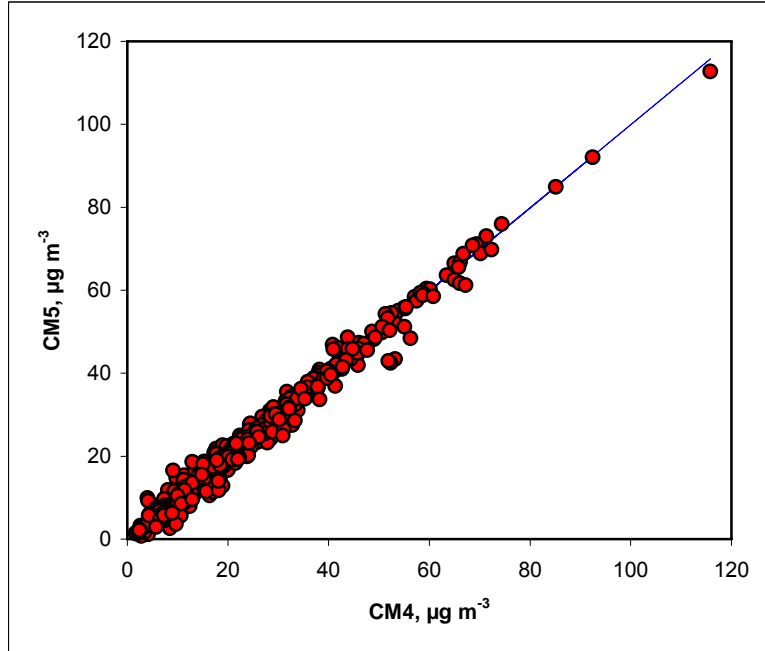**Figure G.1 – CM5 vs. CM4 for all sites**

Table G.2 – Equivalence procedure with all available measurements at all sites separately *:*

		Berlin		**Madrid**		**Vienna**	
REGRESSION OUTPUT							
slope b		1,020		1,000		1,000	
uncertainty of b		0,009	significant	0,046		0,006	
intercept a		-0,81		-0,06		0,54	
uncertainty of a		0,31	significant	0,65		0,25	significant
number of data pairs		65		91		109	
EQUIVALENCE TEST							
random term	µg/m³	0,92		1,82		0,73	
bias at LV	µg/m³	-0,10		-0,05		0,53	
combined uncertainty	µg/m³	0,93		1,82		0,90	
relative uncertainty		2,7%	pass	5,2%	pass	2,6%	pass
ref between-sampler u	µg/m³	0,77		1,49	µg/m³	0,99	
		Rome		**Athens**		**Duisburg**	
REGRESSION OUTPUT							
slope b		1,011		1,408		1,050	
uncertainty of b		0,023		0,073	significant	0,028	
intercept a		-0,81		-6,92		-0,62	
uncertainty of a		0,52		2,19	significant	0,48	
number of data pairs		81		75		133	
EQUIVALENCE TEST							
random term	µg/m³	0,51		8,03		1,91	
bias at LV	µg/m³	-0,43		7,36		1,13	
combined uncertainty	µg/m³	0,66		10,89		2,22	
relative uncertainty		1,9%	pass	31,1%	FAIL	6,3%	pass
ref between-sampler u	µg/m³	1,16		4,82		1,46	
		Vredepeel		**Aspvreten**		**Teddington**	
REGRESSION OUTPUT							
slope b		0,956		1,026		0,963	
uncertainty of b		0,023		0,013		0,014	significant
intercept a		-0,08		0,13		-1,35	
uncertainty of a		0,34		0,28		0,48	significant
Number of data pairs		64		61		63	
EQUIVALENCE TEST							
Random term	µg/m³	1,51		0,57		2,11	
bias at LV	µg/m³	-1,63		1,02		-2,65	
combined uncertainty	µg/m³	2,22		1,17		3,38	
Relative uncertainty		6,3%	pass	3,3%	pass	9,7%	pass
ref between-sampler u	µg/m³	1,03		0,99		1,32	

Equivalence HVS-CM6 vs. LVS-CM4/CM5

For all practical purposes, LVS-CM5 was used to exemplify the designated standard low volume method.

The next tables show the results of the equivalence procedure, collecting together all available measurements at all sites, and per site separately.

When data from all sites are combined, the equivalence criteria are fulfilled. However, for a number of sites individually the equivalence criteria are not fulfilled. The possible reasons for this are discussed in Annex F.

Table G.3 – Equivalence procedure for HVS-CM6 vs. LVS-CM4/CM5 with all available measurements at all sites

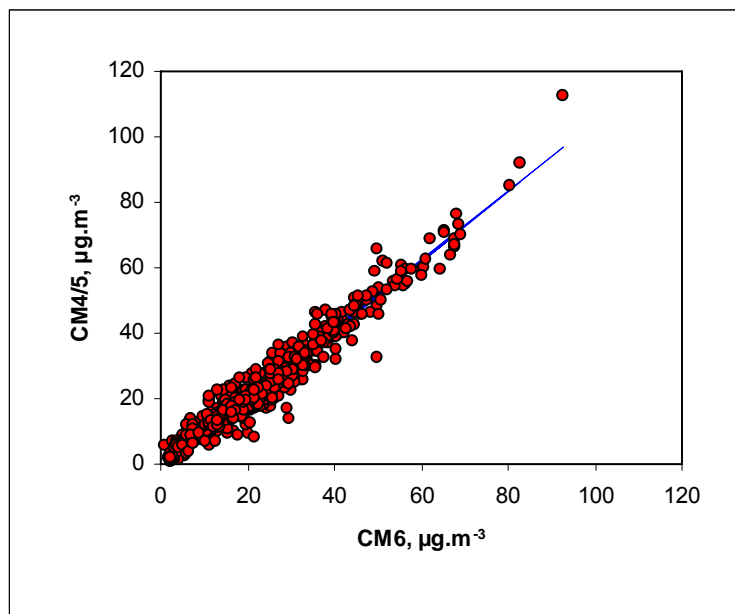|		All sites	
REGRESSION OUTPUT			
slope b		1,050	significant
uncertainty of b		0,010	
intercept a		-0,80	significant
uncertainty of a		0,26	
number of data pairs		608	
EQUIVALENCE TEST			
random term	µg/m³	3,45	
bias at LV	µg/m³	0,95	
combined uncertainty	µg/m³	3,58	
relative uncertainty		10,2%	pass
ref between-sampler u	µg/m³	1,15	

Figure G.2 – CM5 vs. CM6 for all sites

Table G.4 – Equivalence procedure for HVS-CM6 vs. LVS-CM4/CM5 with all available measurements at all sites separately

		Berlin		Madrid		Vienna	
REGRESSION OUTPUT							
slope b		1,067		0,905		1,047	
uncertainty of b		0,012	significant	0,055		0,012	significant
intercept a		0,32		0,34		-2,51	
uncertainty of a		0,39		0,83		0,47	significant
Number of data pairs		66		90		103	
EQUIVALENCE TEST							
Random term	µg/m³	1,42		2,62		2,00	
bias at LV	µg/m³	2,66		-2,99		-0,86	
combined uncertainty	µg/m³	3,02		3,97		2,17	
Relative uncertainty		8,6%	PASS	11,3%	PASS	6,2%	PASS
ref between-sampler u	µg/m³	0,76		1,61		0,75	
		Rome		**Athens**		**Duisburg**	
REGRESSION OUTPUT							
slope b		0,867		0,853		1,228	
uncertainty of b		0,031	significant	0,089		0,037	significant
intercept a		0,16		2,25		-0,92	
uncertainty of a		0,78		2,19		0,72	
Number of data pairs		81		40		41	
EQUIVALENCE TEST							
Random term	µg/m³	1,69		4,19		1,58	
bias at LV	µg/m³	-4,49		-2,88		7,05	
combined uncertainty	µg/m³	4,80		5,09		7,23	
Relative uncertainty		13,7%	FAIL	14,5%	FAIL	20,7%	FAIL
ref between-sampler u	µg/m³	1,01		1,14		0,91	
		Vredepeel		**Aspvreten**		**Teddington**	
REGRESSION OUTPUT							
slope b		1,117		1,270		1,150	
uncertainty of b		0,032	significant	0,056	significant	0,019	significant
intercept a		0,01		-1,86		0,16	
uncertainty of a		0,63		0,70	significant	0,52	
Number of data pairs		60		64		63	
EQUIVALENCE TEST							
Random term	µg/m³	2,47		3,12		2,47	
bias at LV	µg/m³	4,09		7,58		5,42	
combined uncertainty	µg/m³	4,78		8,20		5,96	
Relative uncertainty		13,6%	FAIL	23,4%	FAIL	17,0%	FAIL
ref between-sampler u	µg/m³	0,77		1,57		1,34	

References

[1]   Community Directive 96/62/EC on Ambient Air Quality Assessment and Management

[2]   Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air

[3]   EN 14907:2005, Ambient air quality -- Standard gravimetric measurement method for the determination of the $PM_{2,5}$ mass fraction of suspended particulate matter

[4]   EN 12341:1998, Air quality -- Determination of the PM_{10} fraction of suspended particulate matter - Reference method and field test procedure to demonstrate reference equivalence of measurement methods

[5]   Federal Register, Part II, Environmental Protection Agency, Vol. 62, No. 138, Friday, July 18, 1997.

[6]   Hering, S. and Class, G.: The magnitude of bias in the measurement of $PM_{2,5}$ arising from volatilisation of particulate nitrate from Teflon filters. J. Air & Waste Manage. Assoc. 49:725-733 (1999).

[7]   Eisner, D. and Wiener, R.W.: Discussion and evaluation of the volatility test for equivalency of other methods to the federal reference method for fine particulate matter. Aerosol Science and Technology 36: 433-440 (2002).

[8]   Chow, J. C, Watson, J. G., Lowenthal, D. H. And Magliano, K. L.: Loss of $PM_{2.5}$ nitrate from filter samples in Central California

[9]   Kendall, M.G. and Stuart, A.: The advanced theory of statistics. C. Griffin and Co., London (1969), p. 391-480

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