2^{nd} Interim Report on

Grant Agreement for an Action

SA/CEN/ENTR/503/2011-11

“Ambient Air Quality”

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CEN/TC 264 – “Air Quality”
WG15 – “Particulate Matter (PM_{10}/$PM_{2,5}$)”

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Contents

1. Executive Summary

Directive 2008/50/EC on ambient air quality and cleaner air for Europe sets limit values for particulate matter PM_{10} and fine particulate matter $PM_{2,5}$. The reference measurement methods have already been standardized by ESOs (EN12341:2014), but they are manual/semi-automated methods. A standard for automated PM measurements (Article 32.3) is still missing.

CEN/TS16450:2013 (the technical specification which covers the testing of Automated Measurement Systems for PM) has been transferred to TC264 WG15 in order to formulate a standard. A series of 6 Work Packages were mandated, and a Project Coordinator was appointed. A series of seven meetings were organised, and at least one person from each of the organisations itemised above has attended each meeting (with one apology due to illness and another due to prior commitments), as have WG15 members from other organisations

In order to improve the narrative of the report, the Work Packages are discussed in the order in which they were undertaken, as opposed to number order.

The role of Work Package 6 was to perform a full statistical evaluation of the findings of Work Packages 1 through 5, and to use these in order to propose the revisions to the draft standard that are required in order for it to be published. The herein report forms that deliverable.

Work Package 1 was a stand-alone Work Package linking directly to the revision of the draft Standard. Two organisations won sub packages for WP1: TÜV Rheinland and NPL. The purpose of this Work Package was to test whether three key laboratory test procedures proposed within the draft standard are feasible:

- Dependency on temperature. It was found that it was not possible to undertake a span test on all instruments. A note has been added to the draft Standard to allow that 'If an AMS is not providing a span calibration device or the provided device is not suitable, this must be explicitly pointed out in the type-approval report and in the certification text'. The requirement for monitors intended for outdoor application to be tested at -20 and 50 °C has been removed. Instead a requirement has been added to test 'at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures';
- Dependency on water vapour. Both organisations had difficulty in regulating the %RH provided to the inlet of the instrument, and instead decided to control the humidity of the entire climate chamber. The draft Standard has been modified to add an option to control the humidity of the entire chamber. The requirement to test at 30% RH has been replaced by a requirement to test at 40 % RH;
- Flow rate accuracy. A recommendation to use a flow meter with a low pressure drop has been incorporated. A suggestion to revise the percentage requirement for low flow devices has not been implemented, as the percentage deviation between actual and intended flow is equally critical regardless of the absolute magnitude of the intended flow. Text relating to the temperature ranges as specified in the Section on 'Dependence on Temperature' have been copied to the 'Flow Rate Accuracy' Section.

In Work Package 2 four different research groups tested a variety of automated instruments in order to see if the test criteria listed in CEN/TS 16450:2013 were suitable for incorporation in to the draft standard.

All four organisations followed the equivalence calculations set out in CEN/TS 16450:2013. All four organisations used the official spreadsheet as posted on the Europa website in order to make these calculations. The equations were shown to be very effective in indicating the equivalence of candidate methods with respect to the reference method, and it was not necessary to make any changes in the text of the revised standard.

For some instruments, it is not possible to perform checks on all sensors under field conditions. Based on the findings of Work Package 2, the text of the new standard has been modified to add a note allowing that in these cases checks may be performed in a laboratory room with constant temperature and relative humidity by comparing sensor readings (after stabilisation) with those of reference standards".

With respect to the determination of leaks, CEN/TS 16450:2013 was very proscriptive. Based on the findings of Work Package 2, the text of the new standard has been modified to be more pragmatic.

Based upon the leak test results obtained by the Wiesbaden group, the leak test criterion was changed from 2,0% to 2 %.

As some instruments could fail the criteria when functioning within their normal operating parameters, the Sections on zero, leak and flow rate tests have been modified to require that if the criterion is exceeded, then ' the user shall take any action it judges to be appropriate for the specific situation'.

An extra Section has been added with recommendations on how the user can correct the data if any of the criteria are exceeded.

The results of Work Package 2 also showed that:

- It is not appropriate to use PM_{10} inlets corresponding to the design of EN12341:1998 in industrial areas;
- A 'halo' is seen around the collected filter spot – particular when Emfab filters are used. This is not thought to result in a loss of particulate matter from the filter, and so is not of concern;
- The latest version of the reference method standard: EN12431:2014 requires that filters are weighed in an environment maintained between 19 and 21 °C and between 45 and 55 % RH. All four organisations were able to maintain their weighing room facilities within these limits. This proves that the requirement to store filters between 19 and 21 °C and between 45 and 55 % RH is achievable;
- An earlier draft of EN12431:2014 required that the filters are stored in a controlled temperature between 19 and 21 °C after sampling. In order to verify this, the temperature of the sampled filters should be logged. One of the four groups used versions of the reference method that are modern enough to have this facility. Analysis of the data shows that the filters were retained between 19 and 21 °C throughout. This proves that the requirement to store sampled filters between 19 and 21 °C is achievable.

EN12341:2014 allows for four filter media: Quartz, Glass Fibre, Teflon Coated Glass Fibre and Teflon. Tests undertaken in Work Packages 2, 3, 4 and 5 showed that the most suitable filter media was Emfab (a form of Teflon Coated Glass Fibre). The least suitable media was Tissuquartz (a form of quartz). Working groups 34 (anions and cations) and 35 (EC and OC) have chosen Tissuquartz as their preferred media, and it was hoped that this media would also be the preferred media for weighing. Preconditioning has been seen to improve the effectiveness of many filter media. The filter media data collected as part of this Mandate should be used to guide a future revision of EN12341:2014.

2. Introduction

Directive 2008/50/EC on ambient air quality and cleaner air for Europe sets limit values for particulate matter PM_{10} and fine particulate matter $PM_{2,5}$. The reference measurement methods have already been standardized by ESOs (EN12341:2014), but they are manual/semi-automated methods. A standard for automated PM measurements (Article 32.3) is still missing. In order to ensure better data comparability, validated standard methods are therefore equally required. [Standardization Mandate M/503]

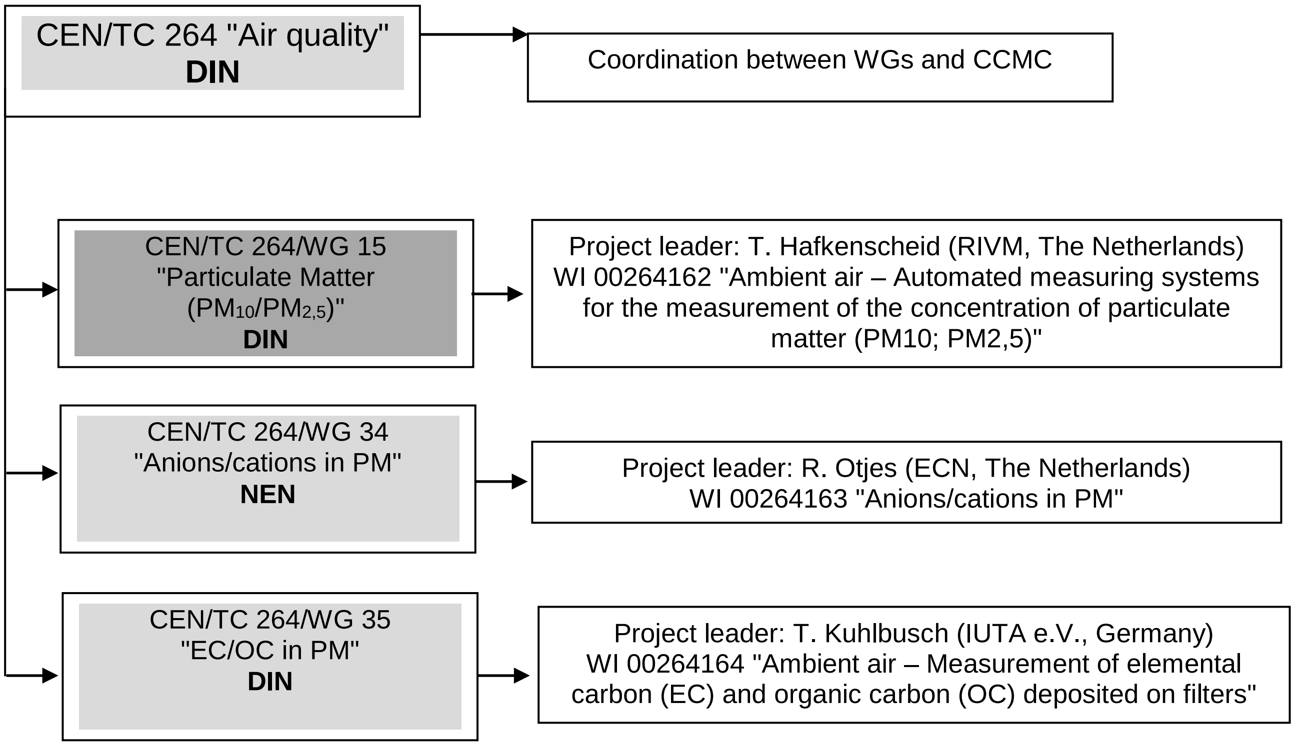
The Member States indicated a need for a standard for automated PM measurements (Article 32.3), as most of the measurements performed today are made by automated methods [Standardization mandate M/503]. This has been dealt with by WG 15 in which 44 experts from 16 countries are involved to perform the standardization and verification work under Mandate M/503.

Three working groups have Work Packages awarded under Mandate M/503: WG15, WG34 and WG35. This report summarises the Work Packages required for the development of standards under WG15.

CEN/TS16450:2013 (the technical specification which covers the testing of Automated Measurement Systems for PM) has been transferred to TC264 WG15 in order to formulate a standard subject to the findings of the herein discussed Work Packages. As the new standard would rely on a comparison to the reference method, M/503 is also being used to advise as to which of the four filter media allowed in EN12341:2014 is most appropriate to be used for equivalence testing.

3. Structure of the work in CEN/TC 264 – Air Quality

In order to perform the work, the following structure was established:



4. Status of the Work Programme

There are a total of 6 Work Packages and a project coordinator split as per the following table.

4.1 Summary

Work Package	Details	Company	Progress
WP1: AMS lab tests	1 of 2	TÜV Rheinland, Germany	Completed
	2 of 2	NPL, United Kingdom	Completed
WP2: Field tests	1 of 4: Traffic site	HLUG, Germany	Completed.
	2 of 4: Industrial site	GGD Amsterdam, The Netherlands	Completed.
	3 of 4: Urban background site	Demokritos, Greece	Completed.
	4 of 4: Rural background site	Ricardo AEA, United Kingdom	Completed.
WP3: Literature review	Literature review on water sorption	RIVM, The Netherlands	Completed
WP4: Humidity tests	Sampling zero air with different levels of humidity	Demokritos, Greece	Completed
WP5: Testing reversibility of water vapour	Reversibility of water vapour sorption	NPL, United Kingdom	Completed
WP6: Statistical evaluation	Data evaluation	Bureau Veritas, United Kingdom	Completed
Project Coordinator	Project Coordinator	RIVM, The Netherlands	Completed

4.2 Meetings

The following meetings have been undertaken, and at least one person from each of the organisations itemised above has attended each meeting (with one apology due to illness and another due to prior commitments), as have WG15 members from other organisations:

- Vienna: 21st May 2013;
- Vienna: 11th July 2013;
- London: 9th December 2013;
- Vienna: 10th April 2014;
- Amsterdam: 14th October 2014;
- Athens: 20th January 2015;
- Rome: 30th and 31st March 2015.

4.3 Reports

A report has been authored for each of the nine groups involved in Work Packages 1 through 5. These are included as an Annex to the present report, which in itself forms the deliverable for Work Package 6. In the following Sections, a summary of the key findings of each report are set out, along with further discussion and statistical analysis.

4.4 Summary of Work Packages

In order to improve readability of this report, the order in which the Work Packages are discussed is:

- Work Package 6;
- Project Coordinator;
- Work Package 1.
- Work Package 3: Which feeds in to Work Package 5;
- Work Package 5: Which feeds in to Work Packages 4 and 2;
- Work Package 4;
- Work Package 2.

4.4.1 Project Coordinator

The role of the Project Coordinator is to coordinate the project and lead discussions in order to elucidate the required deliverables within the proposed schedule, as well as to formulate the draft Standard. The project coordinator has undertaken these responsibilities throughout the project, and has also contributed to the statistical analysis in the herein report. The submission of the draft standard in May 2015 formed the key deliverable associated with this role.

4.4.2 Work Package 6

Work Package 6 requires the assistance of the Project Coordinator in guiding the project in order to elucidate the required deliverables within the proposed schedule. There are two key deliverables. The first of these was to summarise the progress to date as of May 2014. This report was delivered on schedule. The second key deliverable is to perform a full statistical evaluation of the findings of Work Packages 1 through 5, and to use these in order to propose the revisions to the draft standard that are required in order for it to be published. The herein report forms that deliverable.

4.4.3 Work Package 1

Work Package 1 was a stand-alone Work Package linking directly to the revision of the draft Standard. Two organisations won sub packages for WP1: TÜV Rheinland and NPL. For each organisation, a summary report forms the key deliverable, and these are presented in Annex A.

The purpose of this Work Package was to test whether three key laboratory test procedures proposed within the draft standard are feasible:

- Dependency on temperature;
- Dependency on water vapour;
- Flow rate accuracy.

Both organisations tested the same four instruments:

- Grimm Aerosol Technik Model EDM 180, provided by ISSeP, Liège, Belgium;
- Met One Instruments BAM-1020, provided by GGD, Amsterdam, The Netherlands;
- Thermo Fisher Scientific Model 5030 SHARP, provided by HLUG, Wiesbaden, Germany;
- Thermo Fisher Scientific Series 8500C TEOM FDMS provided by UBA Austria, Vienna, Austria.

The tests were first performed by TÜV Rheinland, and then the instruments were transported to NPL. As the two organisations performed the tests in series, it was possible for NPL to adapt their test procedures based upon the findings of TÜV Rheinland.

Key findings of the TÜV Rheinland report are summarised below:

TÜV Rheinland	**Practicality of test methods**	**Feasibility of test criteria**
Dependency on temperature	Practical	Feasible
Dependency on water vapour	Impractical	Feasible
Flow rate accuracy	May be practical if repeated with different flow meters.	A requirement could possibly be inserted for flow meters to have a low pressure drop.

Key findings of the NPL report are summarised below:

NPL	**Practicality of test methods**	**Feasibility of test criteria**
Dependency on temperature	Practical for zero measurements. Limited practicality for span point	Feasible for both zero and span points.
Dependency on water vapour	Practical	Feasible
Flow rate accuracy	Practical	The requirement is achievable for instruments with a flow of 16,7 l min-1, but is harder to achieve for instruments with lower flow rates.

Taking each of the test procedures in turn:

4.4.3.1 Dependency on Temperature

CEN/TS 16450:2013 requires that:

"The dependence of the zero reading and value measured by applying a calibration artefact on the surrounding temperature shall be determined at the following temperatures (within the specifications provided by the manufacturer):

- at a nominal temperature $T_{S,n}$ = 20 °C;
- at a minimum temperature $T_{S,1}$ = 5 °C;
- at a maximum temperature $T_{S,2}$ = 40 °C.

These tests require the use of zero and span calibration devices.

At each temperature setting three individual measurement results at zero and at span should be recorded.

At each temperature setting the criteria for warm-up or stabilisation time are to be met according to 7.4.2.1.

The tests are performed in the temperature sequence $T_{S,n}$ - $T_{S,1}$ - $T_{S,n}$ - $T_{S,2}$ - $T_{S,n}$.

In order to exclude any possible drift due to factors other than temperature, the measurements at $T_{S,n}$ are averaged.

The differences between readings at both extreme temperatures and $T_{S,lab}$ shall be determined.

The differences found shall comply with the performance criteria given in Table 1.

and where the relevant section of Table 1 is:

Performance characteristic	**Requirement**	**Location (Lab/Field)**	**Clause**
Dependence of zero on surrounding temperature[a]	≤ 2,0 µg/m³ from 5 °C to 40 °C for indoor application from -20 °C to 50 °C for outdoor application	L	7.4.7
Dependence of measured value on surrounding temperature[a]	≤ 5 % from the value at the nominal test temperature from 5 °C to 40 °C for indoor application from -20 °C to 50 °C for outdoor application	L	7.4.7

[a] For some AMS the range of operating temperatures is less than the test ranges prescribed in Clauses 7 and 8. In those cases the testing of the dependence of zero and measured value on surrounding temperature should be done according to the manufacturer's operating specifications. Limitations, e.g. operation below or above a certain temperature, shall be specified in the type-approval report."

TÜV Rheinland made a comment that:

"the investigations at the zero point are rather easy and straight-forward to perform, the investigation at the span point are not possible for each instrument due to non-availability of external test standards for the span point. This is especially a known deficit of optical monitors"

TÜV Rheinland declared the test to be both practical and feasible, and made a suggestion to:

“Keep the test method and test criteria for “Dependence of zero and span on surrounding temperature” as described in the Draft Standard”.

NPL found the test to be both practical and feasible for both zero point measurements. While NPL found the method to be feasible for span point measurements, they suggested that it was of limited practicality. This was because of the:

“requirement to have scientific personnel present inside the climate chamber to change artefacts for the measurements, over long periods of time (one hour at each temperature). This included the extremes of temperature between 5 ^{0}C and 40 ^{0}C, which limited the practicality of the method, and could be considered a potential safety hazard”.

In addition, CEN/TS 16450:2013 requires that instruments intended for outdoor operation should be tested at both -20 °C and 50 °C, which are even less appropriate for personal.

The text of the new standard has been amended from that within the existing CEN/TS16450:2013. A few amends relate to making the text more explicit, and a note has been added requiring that the type-approval report and the certification text should clearly state if a span calibration device is not made available. The concerns about performing the span calibrations at -20 °C and 50 °C were discussed in the meeting in Rome in March 2015. TÜV Rheinland noted that they had conducted tests at -20 °C and 50 °C, and that they were therefore practical. The text was however altered to state that tests should be conducted across the range of operating temperatures stated in the instrument manual. Below the text of the new standard is given:

“These tests require the use of zero and span calibration devices.

Note: If an AMS is not providing a span calibration device or the provided device is not suitable, this must be explicitly pointed out in the type-approval report and in the certification text. For this case suitable additional QA actions are to be considered.

The dependence of the zero reading and value measured by applying a calibration artefact on the surrounding temperature shall be determined at the following temperatures:

- at a nominal temperature $T_{S,n}$ = 20 °C;
- at a default minimum temperature $T_{S,1}$ = 5 °C;
- at a default maximum temperature $T_{S,2}$ = 40 °C.
- at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.

At each temperature setting three individual measurement results at zero and at span shall be recorded.

At each temperature setting the criteria for warm-up or stabilisation time are to be met according to 7.4.2.1.

The tests are performed in the temperature sequence $T_{S,n}$ - $T_{S,1}$ - $T_{S,n}$ - $T_{S,2}$ - $T_{S,n}$.

In order to exclude any possible drift due to factors other than temperature, the measurements at $T_{S,n}$ are averaged.

The differences between readings at both extreme temperatures and $T_{S,n}$ shall be determined.

The differences found shall comply with the performance criteria given in Table 1.

and where the relevant section of Table 1 is:

Performance characteristic	Requirement	Location (Lab/Field)	Clause
Dependence of zero on surrounding temperature[a]	≤ 2,0 µg/m^3 – from 5 °C to 40 °C by default for installation in a temperature-controlled environment – at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.	L	7.4.7
Dependence of measured value on surrounding temperature[a]	≤ 5 % from the value at the nominal test temperature – from 5 °C to 40 °C by default for installation in a temperature-controlled environment – at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.	L	7.4.7

[a] Limitations, e.g. operation below or above a certain temperature, shall be specified in the type-approval report.”

4.4.3.2 Dependency on Water Vapour

CEN/TS 16450:2013 requires that:

“The dependence of the AMS readings on the level of water vapour in the sampled air should be determined by supplying humidified zero air to the AMS in excess of the sample flow rate. Tests should be performed by changing the relative humidity of the sampled air between 30 % and 90 %.

These tests require the provision of zero air and an air humidification system. The supply flow rate of humidified air should be ≥ 10 % in excess of the AMS sample flow rate with excess flow being vented.

After stabilisation of relative humidity and AMS reading, a reading over the lowest averaging period of the AMS at 30 % relative humidity is recorded. The relative humidity is then raised back to 90 % at a rate of 30 % per hour. The equilibration time and the average reading are recorded. The humidity is then lowered back to 30 % at a rate of 30 % per h. Again, the equilibration time and the average reading are recorded.

If an instrument provides readings only every 24 h, the rate of changes of humidity should be altered accordingly.

The largest difference in readings between 30 % and 90 % relative humidity should fulfil the performance criterion in Table 1.

and where the relevant section of Table 1 is:

Performance characteristic	**Requirement**	**Location (Lab/Field)**	**Clause**
Effect of humidity on measured value	≤ 2,0 µg/m3 in zero air when cycling relative humidity from 30 % to 90 % and back	L	7.4.9

“

TÜV Rheinland stated:

“CEN/TS 16450:2013 stipulates that the sampled air is first conditioned to 30 % relative humidity, raised back to 90 % relative humidity at a rate of 30 % per hour and then lowered back to 30 % relative humidity. The (zero) readings at the different humidity levels are recorded as well as the (zero) readings during the period of changing the levels under ambient laboratory conditions (20 °C-23 °C). To perform this test, the initial planning was to introduce humidified air in excess to the respective instrument inlet respectively zero filter at top. The humidity content of the technical air will be adjusted by the mean of a water vapour generator. During the test it became obvious, that especially the 90 % relative humidity level couldn´t be kept constant enough due to temperature fluctuations in the laboratory. The ambient temperatures in the lab are within the requirements of table 2 of EN TS 16450 (20-23 °C ±2 °C), but fluctuations of only 1-2 °C can already lead to condensation effects. Based on the obtained experiences it was proposed to test another alternate method as follows:

- The complete systems are running on zero air in the climate chamber at 20 °C;
- The RH content in the chamber will be varied between 30 % and 90 % at 20 °C and the zero readings will be recorded”.

By changing the methodology, TÜV Rheinland were able to control humidity in a way that allowed the test procedures to be fulfilled.

NPL adapted their test procedure to also alter the humidity of the entire climate chamber. While it was possible to create a 30 % RH environment, the humidity was unstable.

In Work Package 4, Demokritos needed to introduce 90 % RH air to a filter sampler. This was not possible at the high flow rates required. In order to get around this, the requirement was reduced from 90 % to 80 %.

The text of the new standard has been amended from that within the existing CEN/TS16450:2013. Many of the amends relate to making the text more explicit. In addition to the preferred option of introducing humidified air to the inlet of each instrument, a second option to control the humidity of the entire chamber was added. Given the different range of problems used by the three organisations (TÜV Rheinland, NPL and Demokritos) in maintaining a constant humidity level, it is clear that the criteria are achievable, but that it is highly dependent on the method each organisation uses to generate constant humidity atmospheres. This was discussed at the meeting in Rome in March 2015, and it was decided to increase the 30 % RH requirement to 40 % RH. Below the text of the new standard is given:

"The dependence of the AMS concentration readings on the level of water vapour in the sampled air shall be determined by supplying humidified zero air to the AMS in excess of the sample flow rate. Tests shall be performed by changing the relative humidity of the sampled air between 40 % and 90 %.

The test can be performed with two general methods:

1) (only) Sampling air humidified (preferred option)

These tests require the provision of zero air and an air humidification system. The supply flow rate of humidified air shall be ≥ 10 % in excess of the AMS sample flow rate with excess flow being vented.

2) Complete surrounding atmosphere humidified.

These tests require a climate chamber in order to provide an atmosphere with varying relative humidities. The AMS shall be completely installed in the chamber and will sample zero air.

For both methods:

After stabilisation of relative humidity and AMS concentration reading, a reading over the lowest averaging period of the AMS at 40 % relative humidity is recorded. The relative humidity is then raised to 90 % at a rate of 25 % per hour. The equilibration time and the average concentration reading are recorded. The humidity is then lowered to 40 % at a rate of 25 % per hour. Again, the equilibration time and the average concentration reading are recorded.

If an instrument provides readings only every 24 hours, the rates of changes of humidity shall be adapted proportionally.

The largest difference in readings between 40 % and 90 % relative humidity shall fulfil the performance criterion in Table 1.

and where the relevant section of Table 1 is:

Performance characteristic	**Requirement**	**Location (Lab/Field)**	**Clause**
Effect of humidity on measured value	≤ 2,0 µg/m³ in zero air when cycling relative humidity from 40 % to 90 % and back	L	7.4.9

"

[a] Limitations, e.g. operation below or above a certain temperature, shall be specified in the type-approval report."

4.4.3.3 Flow Rate Accuracy.

CEN/TS 16450:2013 requires that:

"The mean flow rate should be measured at two temperatures of surrounding air: 5 °C and 40 °C using a reference flow meter. The reference flow meter should have a relative expanded uncertainty (95 % confidence) of ≤ 1,0 % of the controlled flow rate. At each temperature at least 10 measurements should be taken for a minimum period of one hour at the operational flow rate specified by the manufacturer. The measurements should be performed at equal intervals over the measurement period. For each temperature the mean of the measurement results should be compared with the operational flow rate.

The relative difference between the two values should fulfil the performance requirement in Table 1."

and where the relevant section of Table 1 is:

Performance characteristic	**Requirement**	**Location (Lab/Field)**	**Clause**
Flow rate accuracy	≤ 2,0 %	L	7.4.4

"

TÜV Rheinland had difficulty in achieving both the practicality and feasibility of the test criterion, and made a suggestion to:

"Initiate further investigations for "Flow rate accuracy" with another type of reference flow meter with a low pressure drop (e.g. a thermal mass flow meter) and with checked sensors for the flow control to verify if the found deviations are instrument-related only or also related to the used reference flow meter."

NPL used a reference flow meter with a low pressure drop and found that the test procedure was practical. However, they noted that:

"the feasibility was dependent on instrumentation under test because a 2% deviation in flow rate from the nominal of 16.67 l min^{-1} of the Met One BAM-1020, Model 5030 SHARP and the Series 8500C TEOM FDMS is relatively easy to fulfil. A 2% deviation in flow rate from the nominal value of 1.2 l min^{-1} for the Model EDM 180 Grimm is more stringent".

The text of the new standard has been amended from that within the existing CEN/TS16450:2013. Amends relate to making the text more explicit. The suggestion to use a flow meter with a low pressure drop has been incorporated. The suggestion to revise the percentage requirement for low flow devices has not been implemented, as the percentage deviation between actual and intended flow is equally critical regardless of the absolute magnitude of the intended flow. Text relating to the temperature ranges as specified in the Section on 'Dependence on Temperature' have been copied to the 'Flow Rate Accuracy' Section. Below the text of the new standard is given:

"The mean flow rate shall be measured at two temperatures of surrounding air:

- 5 °C and 40 °C by default
- at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures; these temperatures shall then be specified in the type-approval report.

The measurements shall be performed using a reference flow meter having a relative expanded uncertainty (95 % confidence) of ≤ 1,0 % of the controlled flow rate.

NOTE It is recommended to use a low pressure-drop flow meter.

At each temperature, at least 10 independent measurements shall be taken over a minimum period of one hour at the operational flow rate specified by the manufacturer. The measurements shall be performed at equal intervals over the measurement period. For each temperature, the mean of the measurement results shall be compared with the operational flow rate.

The relative difference between the two values shall fulfil the performance requirement in Table 1.

and where the relevant section of Table 1 is:

Performance characteristic	**Requirement**	**Location (Lab/Field)**	**Clause**
Flow rate accuracy[a]	≤ 2,0 % – at 5 °C and 40 °C by default for installation in a temperature-controlled environment – at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.	L	7.4.4

“

4.4.4 Work Package 3

Work Package 3 required an in depth summary of the white and grey literature that was available in relation to the water sorption of filters. The summary report forms the key deliverable, and is given in Annex A.

25 appropriate references were located. A relatively large amount of information is available for Whatman QMA quartz-fibre filters, most likely because these have been quite extensively used throughout the European Union for reference measurements. Other filters for which more systematic studies have been performed include Pall Tissuquartz, Pall Teflo and Pall Emfab. For most other filters no information, or only information from isolated experiments, is available.

Summarising, based on the information currently available, the following conclusions may be drawn:

- Quartz-fibre filters have problems due to significant sorption of water vapour, although their behaviour may improve when the filters are preconditioned to high relative humidities before the regular conditioning procedure. The report concludes that they are generally less suited than other media for use in reference measurements of particulate matter, though other factors need to be considered when choosing an appropriate filter media.
- Teflon and teflon-coated glass-fibre filters show little interaction with water vapour, making them better suited for use in reference measurements of particulate matter;
- Less information exists for glass-fibre filters.

The findings of Work Package 3 were used to decide the filter media used in Work Package 5.

4.4.5 Work Package 5

The purpose of Work Package 5 was to test the adsorption effects of different filter media. This was achieved by weighing different filter media at a series of varying relative humidities at a constant temperature. In order to choose the filter media tested, the findings of Work Package 3 were fed in to Work Package 5. In turn, the findings of Work Package 5 were fed in to Work Packages 4 and 2. The summary report forms the key deliverable, and is given in Annex A.

EN12341:2014 allows for four filter media: Quartz, Glass Fibre, Teflon Coated Glass Fibre and Teflon. Based upon the findings of Work Package 3, the following materials were tested across two different test runs:

- Emfab (Teflon coated glass fibre);
- Pre conditioned Emfab (Teflon coated glass fibre - Second test run only);
- FibreFilm (Teflon coated glass fibre);
- GF10 (Glass fibre);
- Pre Conditioned GF10 (Glass fibre);
- Munktell (Glass fibre);
- Pre Conditioned Munktell (Glass fibre);
- MTL Perfluoroalkoxy (PFA) ring supported PTFE (Teflon);
- QMA (Quartz);
- Pre Conditioned QMA (Quartz);
- Tissuquartz (Quartz - also known as ultrapure quartz (QUP));
- Pre Conditioned Tissuquartz (Quartz)
- Whatman unsupported PTFE (Teflon - Second test run only);

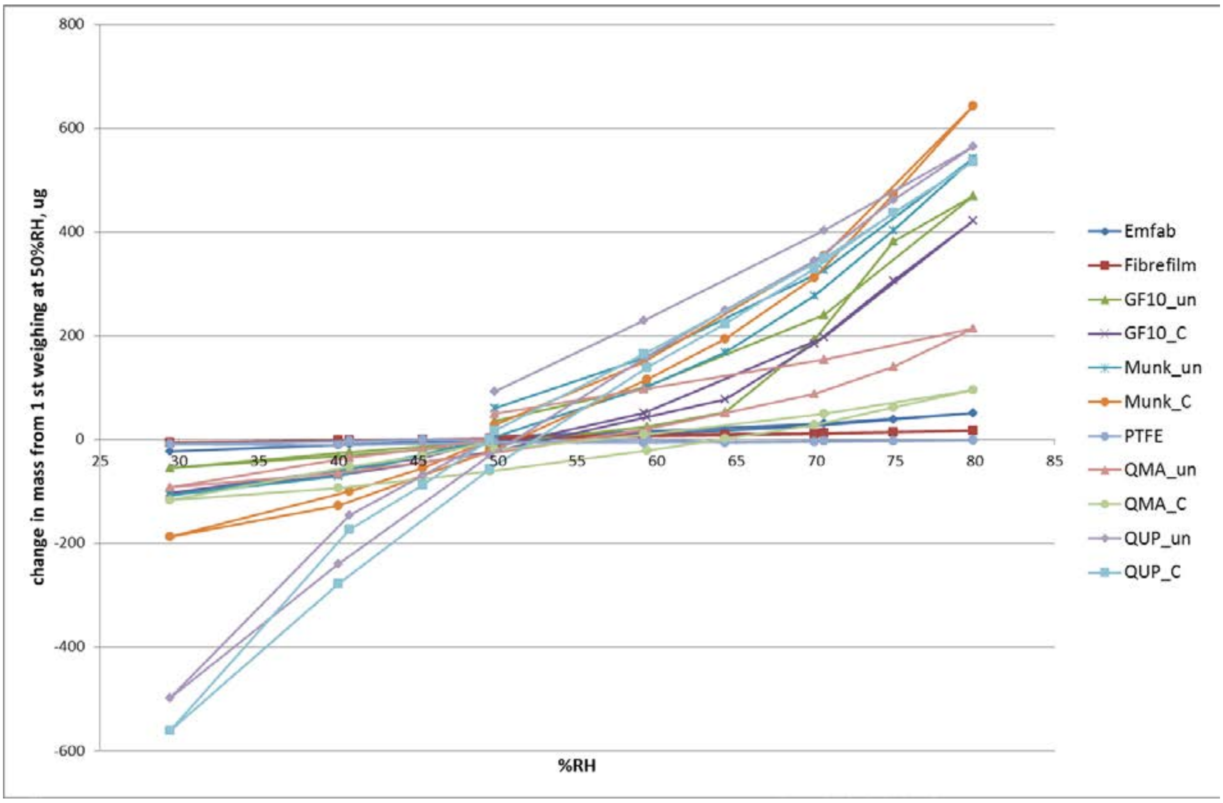
Where required, filters were preconditioned by GGD in Amsterdam. The filters were removed from their packages and placed in stacks of 7-8 to plastic containers. They were then placed in a desiccator inside GGD's weighing room kept at stable conditions of 20 C and 50% RH. Instead of a dessicant, the desiccator contained water. The filters were stored for 25 days in the desiccator, and then were placed in their original package, as delivered. The filters were transferred to NPL in a cool box. The temperature during transport remained between 10 and 20 °C. A picture of the desiccator and the filters is below:

4.4.5.1 Test Run 1

The first test went from 50% RH to 30 % RH then 80 % RH before dropping to 30 % RH; and had the following relative humidity program:

- 50%RH;
- 45%RH;
- 40%RH;
- 30%RH;
- 40%RH;
- 50%RH;
- 60%RH;
- 65%RH;
- 70%RH;
- 75%RH;
- 80%RH;
- 70%RH;
- 60%RH;
- 50%RH;
- 45%RH;
- 40%RH;
- 30%RH.

A graph of the change in mass as a function of Relative Humidity of each filter type is shown below:



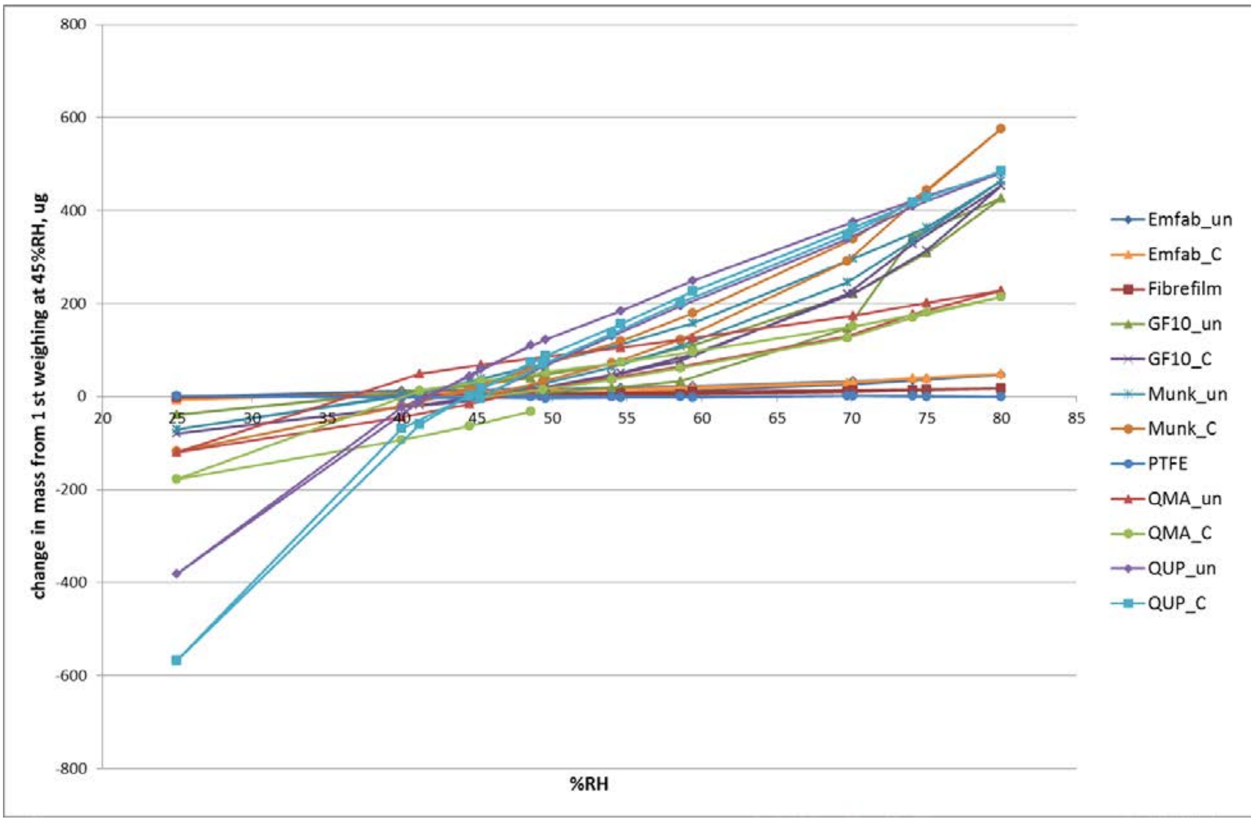
Graphs showing each media in detail are presented in the NPL report included in Annex A.

4.4.5.2 Test Run 2

The second test was operated in the opposite direction and went from 45% RH to 80 % RH then dropping to 30 % RH before rising again to 50 % RH; and had the following relative humidity program:

- 45%RH;
- 50%RH;
- 55%RH;
- 60%RH;
- 70%RH;
- 75%RH;
- 80%RH;
- 75%RH;
- 70%RH;
- 60%RH;
- 55%RH;
- 50%RH;
- 45%RH;
- 40%RH;
- 30%RH;
- 40%RH;
- 45%RH;
- 50%RH.

The general pattern of the first set of tests was very similar to the on-going second test, indicating that changing the order of the relative humidity program made little difference.



Graphs showing each media in detail are presented in the NPL report included in Annex A.

4.4.5.3 Interpretation of Results

For each filter the overleaf diagram shows the relative change from the first weighing for all weighings at either 45 or 50 % RH as a box and whisker plot. These humidities are chosen as the required upper and lower limits specified in EN12341:2014.

In order for the filter to be considered acceptable, then every single mass should be between minus 60 µg and 60 µg (the repeatability criteria of repeat weighings of sampled filters in EN12341:2014).

Whatman unsupported PTFE filters curled up considerably and could not be weighed in the robot weighing mechanism used for this study.

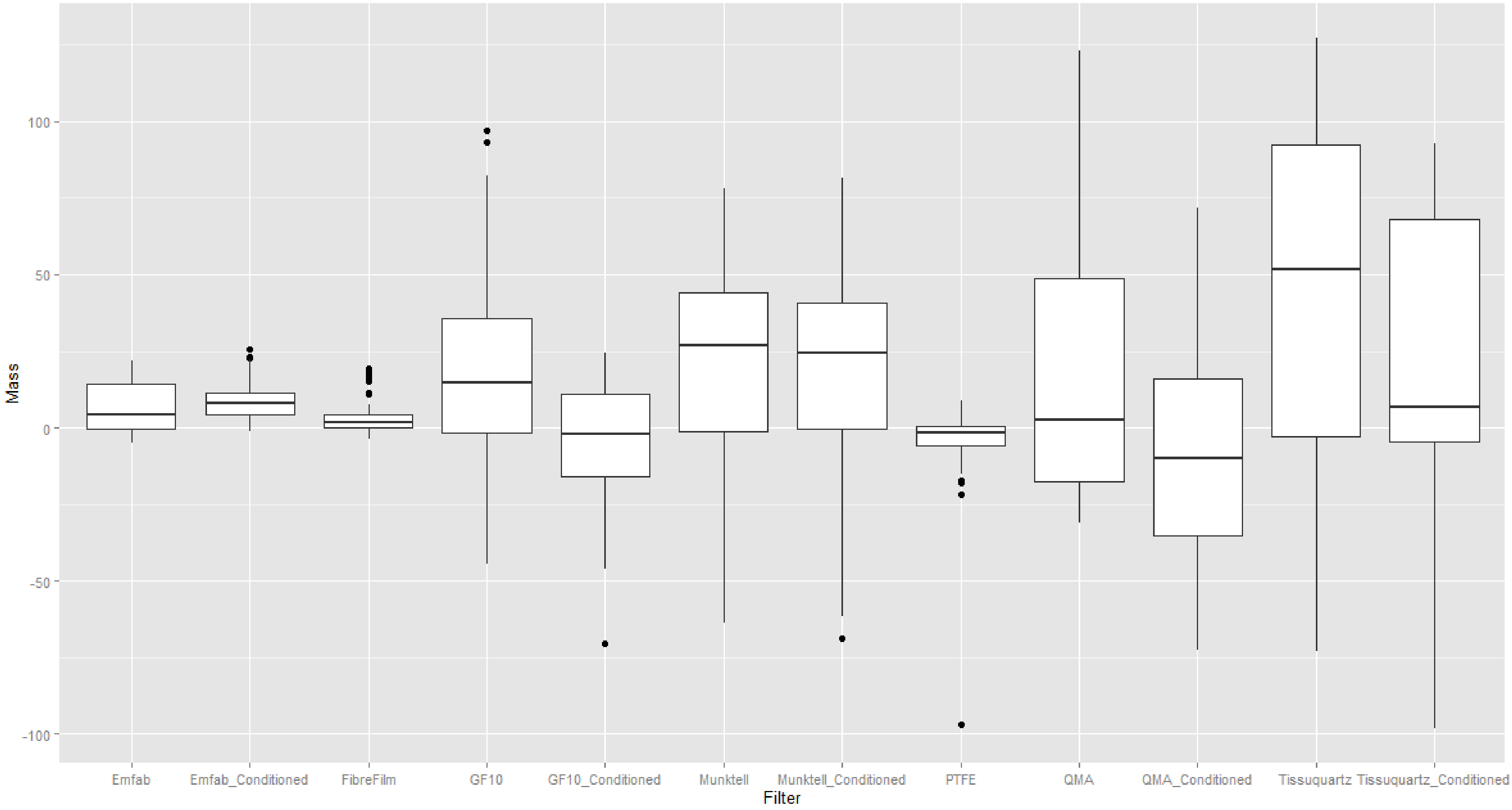
Emfab, MTL PFA ring supported Teflon and Fiberfilm all pass the ±60 µg criterion (after the removal of an outlier for Teflon that was potentially caused by static effects).

Of these, MTL PFA ring supported Teflon is the US reference material, but it has a low sample loading and it is believed that it would clog in the European Reference Method where the flow rate is 2.3 times that of the US method. The manufacturer of both the balance and the PFA ring supported Teflon filters (MTL) was consulted about the static effects. The response was that it is necessary to use both a faraday cage and polonium source to effectively remove all static effects. As polonium is restricted in the UK, only a faraday cage is currently being used. MTL also reported that other ring supported Teflon media are available that use PMP instead of PFA. While PFA is inert, PMP is reversibly water adsorbent and creates a mono layer of water on the ring. Additionally PMP irreversibly adsorbs organics and filters have been shown to gain 30 µg a month. Conversely however, PMP is less prone to static effects than is PFA.

Emfab is used in the UK network and for equivalence testing in the UK and Germany. It performs well, but under extremely heavily polluted or foggy days, it may clog when operated in the reference method. It does not clog when used in samplers at the lower US reference method flow rate. Fiberfilm has a higher porosity than Emfab, and while it looks promising, there is concern about particulate breakthrough.

The conditioned and unconditioned filters from each of Munktell, GF10 and QMA are all at around the 60 µg mark, and could be interpreted as either passing or failing this test. Of these, only unconditioned QMA and conditioned GF10 had an average close to zero. Use of the other filter materials would lead to a systematic bias in measurements. These filter materials are used in numerous European networks.

The conditioned and unconditioned Tissuquartz fails on the 60 µg criterion. Working groups 34 (anions and cations) and 35 (EC and OC) have chosen Tissuquartz as their preferred media, but it is unfortunately not suitable for PM mass measurements without a significant reduction in data quality.


100
50
0
-50
-100
Mass
Emfab
Emfab_Conditioned
FibreFilm
GF10
GF10_Conditioned
Munktell
Munktell_Conditioned
PTFE
QMA
QMA_Conditioned
Tissuquartz
Tissuquartz_Conditioned
Filter

Further interpretation has been undertaken by the Project Coordinator.

For Test Run 1, the results from these experiments were used to calculate the differences between average masses at 45 %RH with relative humidity decreasing, and:

- 50 %RH, respectively 55 %RH, with relative humidity increasing;
- 55 %RH, respectively 50 %RH, with relative humidity decreasing after having been at 80 %RH.

As no weighings were performed at 55% RH during Test Run 1, the masses were calculated *via* linear interpolation of weighings performed at 50 and 60 % RH.

For Test Run 2, the results from these experiments were used to calculate the differences between average masses at 45 %RH with relative humidity increasing, and:

- 55 %RH, respectively 50 %RH, with relative humidity decreasing;

These results are shown in the overleaf Table.

From these results it is observed that:

- PTFE and PTFE-coated glass-fibre filters do not show a significant irreversible uptake of water vapour
- Whatman GF10 and quartz-fibre filters sorb significant masses of water vapour, with pure quartz-fibre filters showing the highest irreversible sorption
- Preconditioning appears to have an effect on the sorbed mass of water vapour for Whatman GF10 and Whatman QMA, and, to a lesser extent for Pall Tissuquartz; for the latter filter the mass sorbed is not reduced to acceptable levels, e.g., to < 60 µg
- Apparently the presence of glass (fibre) is responsible for the effects of preconditioning on the Whatman GF10 and QMA filters (QMA contains approximately 5% glass binder). Emfab is glass fibre with a layer of Teflon on top.
- The reduction of the permitted relative humidity for conditioning and filter weighing from 45 %RH – 55 %RH to 45 %RH – 50 %RH considerably reduces the mass of water sorbed.
- For the second test run, the effect of preconditioning on the water uptake of the Whatman filters appears less pronounced than for the first test run.

From these results it is concluded that when considering the (irreversible) sorption of water vapour, the PTFE and PTFE-coated filters behave well. The Whatman GF10 glass-fibre filter and Whatman QMA quartz-fibre filter may be suitable for use when preconditioned by exposure to a high-humidity atmosphere for several weeks. The pure quartz-fibre filters appear to be less suitable due to their high, irreversible uptake of water vapour.

Filter Type	Test Run 1 Pass 1 in µg			Test Run 1 Pass 2 in µg			Test Run 2 Pass 1 in µg		
	Difference 45 %RH↓ and 50 %RH↑	**Difference 45 %RH↓ and 55 %RH↑**	**Difference between regimes**	**Difference 45 %RH↓ and 55 %RH↓**	**Difference 45 %RH↓ and 50 %RH↓**	**Difference between regimes**	**Difference 45 %RH↑ and 55 %RH↓**	**Difference 45 %RH↑ and 50 %RH↓**	**Difference between regimes**
Emfab	3	9	6	15	10	5	19	16	3
Fibrefilm	2	5	3	8	7	1	8	6	2
Pall Teflo	-6	-3	3	-6	-6	0	-3	-4	1
Whatman GF10	4	21	17	81	49	32	75	49	26
Whatman GF10 preconditioned	10	40	30	49	19	30	51	22	29
Munktell quartz	31	87	56	140	89	51	113	73	40
Munktell quartz preconditioned	32	102	70	143	83	60	120	71	49
Whatman QMA	-10	14	24	91	67	34	106	87	29
Whatman QMA preconditioned	-29	-9	20	27	12	25	75	54	21
Pall Tissuquartz UP	39	155	116	270	162	108	187	124	63
Pall TQ preconditioned	31	129	98	179	105	74	160	92	68

4.4.6 Work Package 4

The purpose of this Work Package was to study the effect of sampling zero air with different levels of humidity and comparing the results with levels of field blank media. For this purpose, samplers were placed in a temperature controlled climate chamber and sampled humidified zero air. Three levels of relative humidity were used: 20, 50 and 80 % RH. The results of Work Package 5 were used in order to decide which filter media should be tested in Work Package 4. The summary report forms the key deliverable, and is given in Annex A.

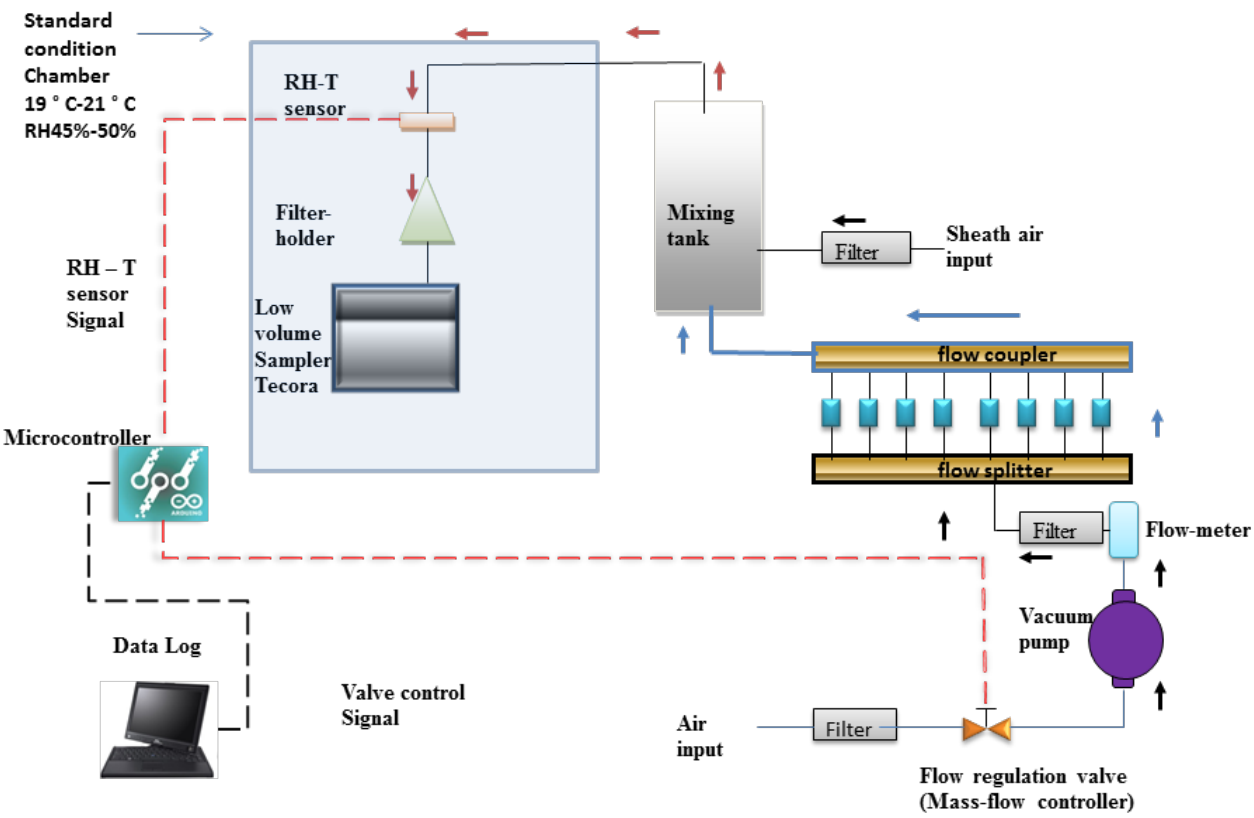
CEN/TS 16450:2013 specifies that tests are undertaken at 90 % RH. Demokritos initially had concerns about the ability to provide a constant high humidity in their tests, and an allowance was made to conduct these tests at 80%. These concerns are similar to those experienced by both test houses undertaking tests under Work Package 1 (See earlier in the herein report).

The following filter media were tested:

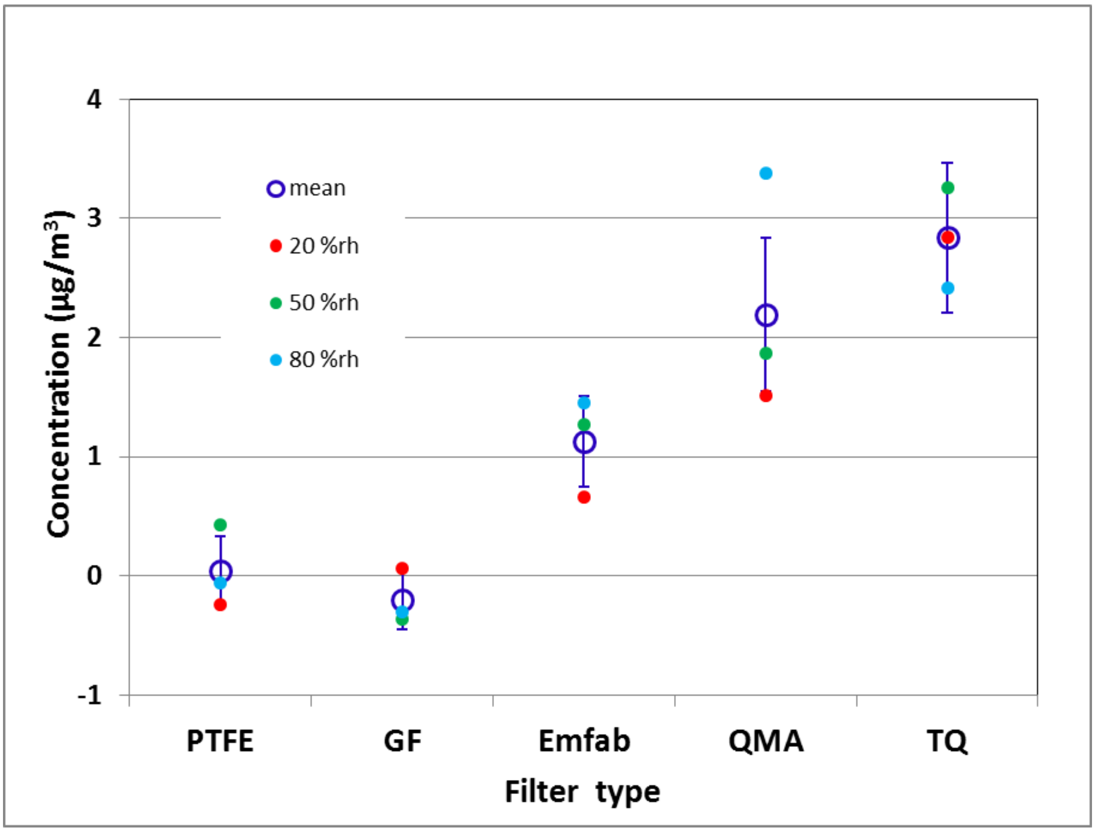
- Emfab;
- GF10 Unconditioned;
- Whatman QMA Conditioned;
- Whatman PTFE;
- Pall Tissuquartz Unconditioned.

For the measurements a Low volume sampler TCR Tecora was used. The sampler was sampling at a flow rate of 2,3 m³/h for 24 hours. Filters were weighed in accordance with the requirements set out in EN 12341:2014. For each Relative Humidity and each filter type we repeated the measurement at least three times.

Owing to the requirements to introduce a wide range of humidities, it was necessary to change the setup of the system for each set of experiments. For example, the below diagram shows how the equipment was set up for measurements at 80 % RH:



The below graph shows the average for each set of filter media and %RH:



Uncertainty calculations were undertaken by the Project Coordinator. The methodology employed in the calculation of the error bars was:

1. The numbers of experiments for the three relative humidities varied. Therefore the number per filter per relative humidity were reduced to three by leaving out the extreme values;
2. The mean and standard deviation of the mean (SD divided by the square root of 9) we calculated;
3. The 95% confidence interval was calculated by multiplying the SD_mean by 2,31.
4. No component for the weighing uncertainty was included, as this is small and is further reduced by the number of experiments.

The results of this Work Package were surprising when compared to those of Work Package 2 (See next Section), Work Package 3 (See earlier), and Work Package 5 (See later), in that the deviation from zero of Emfab was greater than expected, and the deviation from zero of unconditioned GF10 was smaller than expected.

4.4.7 Work Package 2

4.4.7.1 Introduction

The purpose of Work Package 2 was to test the field test procedures listed in CEN/TS 16450:2013, and to decide on their suitability for inclusion in the new standard. There is an additional requirement to field test filter materials. The results of Work Package 5 were used in order to decide which filter media should be tested in Work Package 2. Additional parameters monitored during the campaigns were also useful in providing insights in to the potential future amendment of EN12341:2014. Four organisations were awarded contracts under Work Package 2. For each organisation, the summary report forms the key deliverable, and is given in Annex A.

A summary of the instruments tested is:

Classification	Organisation	Country	Reference Method	Candidate Methods
Rural	Ricardo AEA	UK	2 PM_{10} SEQ 47/50s manufactured by Sven Leckel GMBH	1 PM_{10} TEOM FDMS with CB type drier.
Traffic	HLUG	Germany	2 PM_{10} SEQ 47/50s manufactured by Sven Leckel GMBH	1 PM_{10} Sharp 5030.
Industrial	GGD	The Netherlands	2 PM_{10} LVS 3.1s manufactured by Comde Derenda GMBH	1 PM_{10} BAM 1020; 1 PM_{10} FAI SWAM (with the ability to use both 1 l min^{-1} and 2,3 l min^{-1} heads); 1 PM_{10} TEOM FDMS with C type drier.
Urban Background	Demokritos	Greece	2 PM_{10} LVS 3.1s manufactured by Comde Derenda GMBH	1 PM_{10} TEOM FDMS with C type drier.

Reference method filter media used in normal operations by the four groups are:

- Ricardo AEA: Emfab
- HLUG: GF10 Unconditioned
- GGD: Whatman QMA Conditioned.
- Demokritos: Whatman PTFE

These media were used in one of the two reference methods located at each site. Based on the results of Work Packages 3 and 5 (discussed earlier in this report), the second reference method for each site was operated with Emfab filters. All the Emfab filters were provided from a single batch by Ricardo-AEA. At the Ricardo AEA site, where Emfab is already the default filter media, the second reference method was alternated between Fiberfilm and unconditioned Tissuquartz.

4.4.7.2 Comparison of Filter Media

A comparison of filter media has been performed by the Project Coordinator. From the results submitted data pairs have been removed using the following procedure.

1. Calculation of the ratio of the result for the “other” filter to that of the Emfab filter.
2. Calculation of the GM and GSD of the ratios.
3. Calculation of the “3-sigma” intervals for the ratios from the GM and GSD.
4. Removal of data pairs for which the ratio is outside the ± 3*sigma interval.

This methodology differs from the Grubbs’ Test methodology in CEN/TS16450:2013.

The results of the regressions and equivalence evaluations according to CEN/TS16450:2013 are presented in the five figures overleaf, and are summarised in the below table. Results marked in bold red indicate significant differences (95% confidence) of either slope or intercept from 1 or 0 respectively.

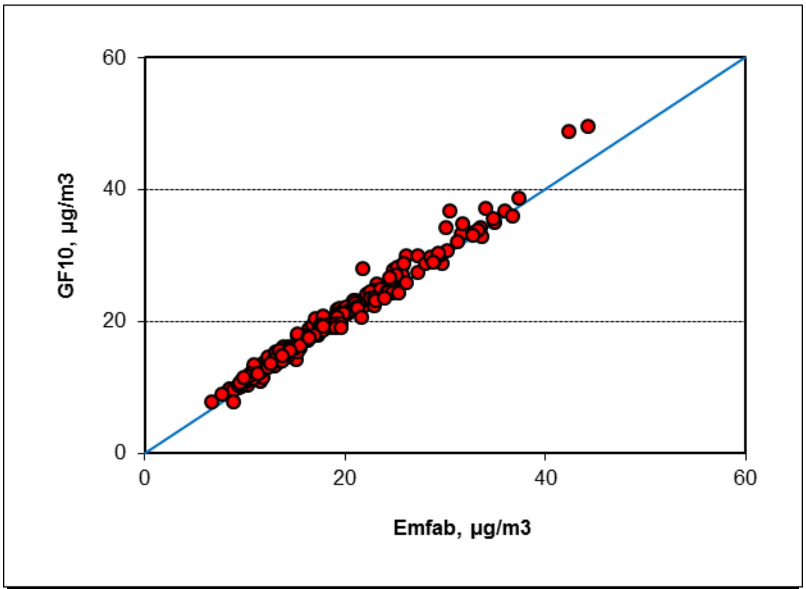
Filter Type	Nr. Data	Mean Emfab	Ratio means Filter/Emfab	Slope (filter = y)	Intercept (filter = y)
Whatman GF10	198	19,2	1,060	**1,037**	0,44
Whatman QMAp	96	25,0	1,035	1,004	**0,77**
Whatman PTFE	93	18,3	0,986	0,967	0,35
Pall Tissuquartz	69	12,2	1,052	0,985	**0,81**
Pall Fiberfilm	52	10,4	1,001	0,975	0,27

The figures and the summary in the table show that:

- Concentrations observed during the comparisons are generally low;
- Comparability of the results of Emfab with PTFE and Fiberfilm are good, with ratios of means close to 1 and regression equations not significantly different from y = x;
- Filters (mainly) consisting of inorganic materials Whatman GF10, Whatman QMA – preconditioned, Pall Tissuquartz QAT UP) yield higher concentrations than Emfab, with significant differences observed in either regression slope or intercept.

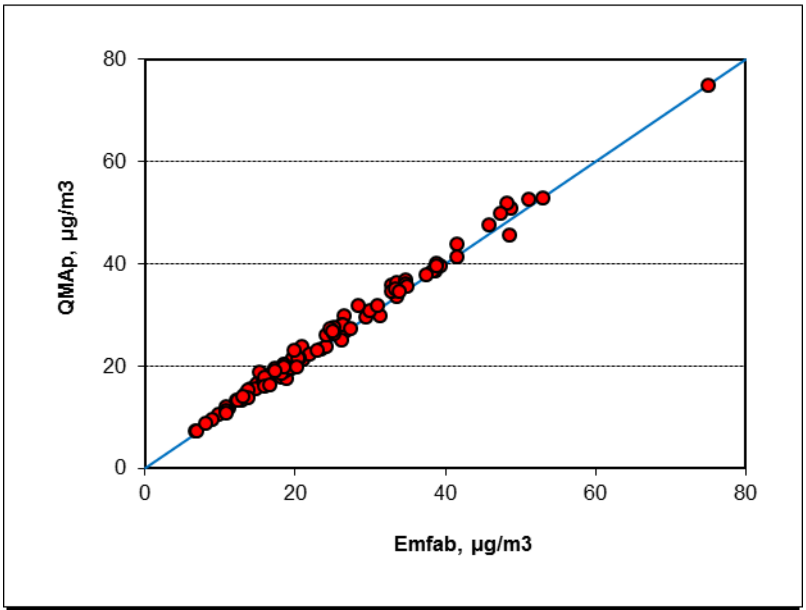
Unfortunately, because of the relatively low concentrations, no observations can be made about the comparability for higher levels of PM_{10}. At the higher levels more pronounced differences may be expected because of the difference in the nature (composition) of the filters.

Figure. Results for the GF10 filter / traffic site.
The blue line represents the y = x relationship.



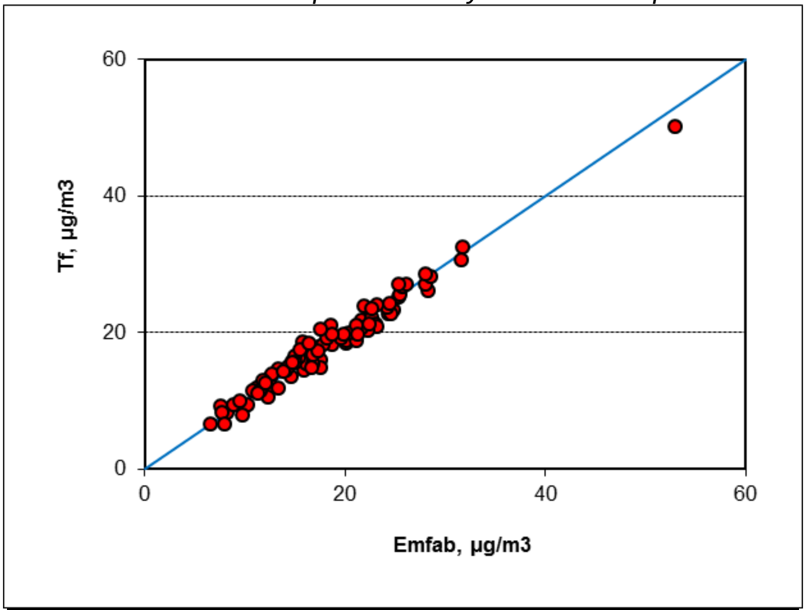
REGRESSION OUTPUT		
slope b	1,037	
uncertainty of b	0,011	significant
intercept a	0,44	
uncertainty of a	0,23	
number of data pairs	198	
r^2	0,98	
EQUIVALENCE TEST RESULTS		
random term	0,81	µg/m³
bias at LV	2,3	µg/m³
combined uncertainty	2,4	µg/m³
relative uncertainty	4,9%	
ref uncertainty	0,8	µg/m³
limit value	50	µg/m³

Figure. Results for the QMAp filter / industrial site.
The blue line represents the y = x relationship.



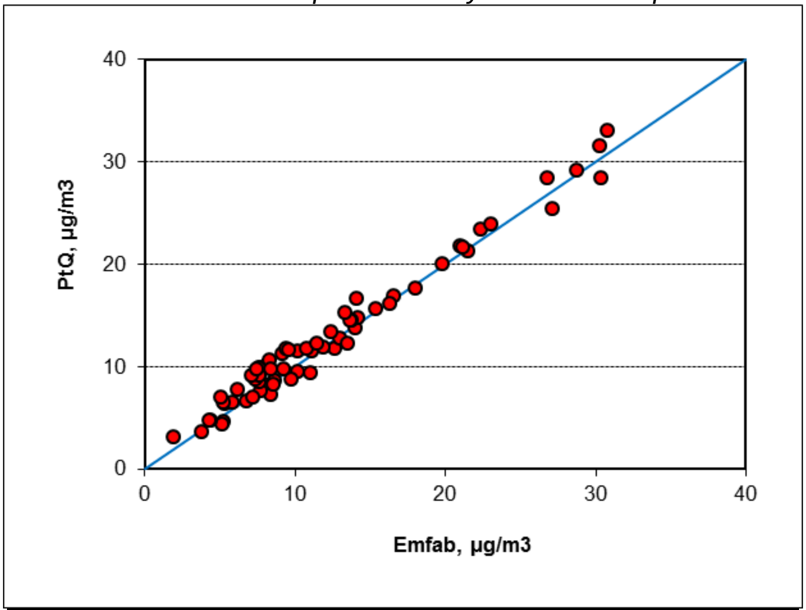
REGRESSION OUTPUT		
slope b	1,004	
uncertainty of b	0,010	
intercept a	0,77	
uncertainty of a	0,27	significant
number of data pairs	96	
r^2	0,99	
EQUIVALENCE TEST RESULTS		
random term	0,83	µg/m³
bias at LV	1,0	µg/m³
combined uncertainty	1,3	µg/m³
relative uncertainty	2,6%	
ref uncertainty	0,8	µg/m³
limit value	50	µg/m³

Figure. Results for the PTFE filter / urban background site.
The blue line represents the y = x relationship.



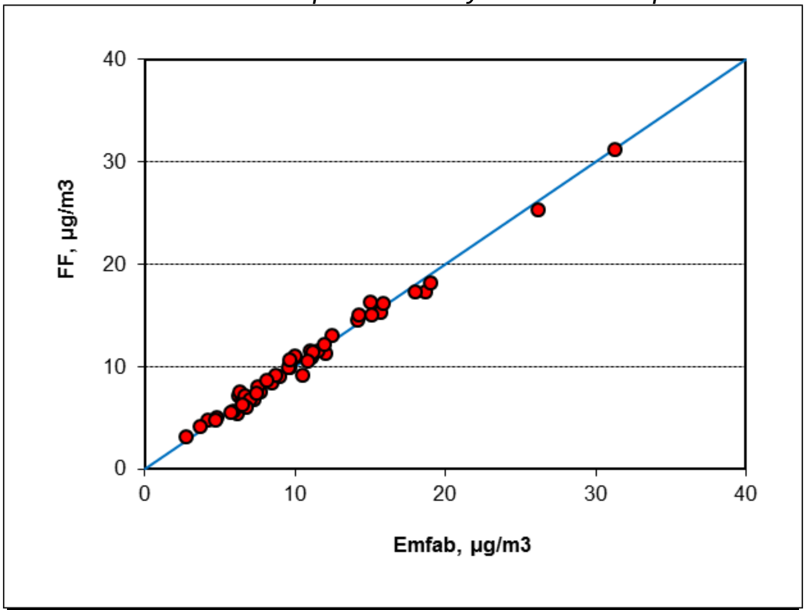
REGRESSION OUTPUT		
slope b	0,967	
uncertainty of b	0,019	
intercept a	0,35	
uncertainty of a	0,36	
number of data pairs	93	
r^2	0,97	
EQUIVALENCE TEST RESULTS		
random term	0,89	µg/m³
bias at LV	-1,3	µg/m³
combined uncertainty	1,6	µg/m³
relative uncertainty	3,1%	
ref uncertainty	0,9	µg/m³
limit value	50	µg/m³

Figure. Results for the Tissuquartz filter / rural site.
The blue line represents the y = x relationship.



REGRESSION OUTPUT		
slope b	0,985	
uncertainty of b	0,019	
intercept a	0,81	
uncertainty of a	0,27	significant
number of data pairs	69	
r^2	0,98	
EQUIVALENCE TEST RESULTS		
random term	0,76	µg/m³
bias at LV	0,1	µg/m³
combined uncertainty	0,8	µg/m³
relative uncertainty	1,5%	
ref uncertainty	0,8	µg/m³
limit value	50	µg/m³

Figure. Results for the Fiberfilm filter / rural site.
The blue line represents the y = x relationship.



REGRESSION OUTPUT		
slope b	0,975	
uncertainty of b	0,015	
intercept a	0,27	
uncertainty of a	0,18	
number of data pairs	52	
r^2	0,99	
EQUIVALENCE TEST RESULTS		
random term	0,43	µg/m³
bias at LV	-1,0	µg/m³
combined uncertainty	1,1	µg/m³
relative uncertainty	2,1%	
ref uncertainty	0,4	µg/m³
limit value	50	µg/m³

In addition to using the methodologies listed in CEN/TS 16450:2013, a comparison of filter media has been made by modelling the differences between the results for the “other” filter and Emfab and examining their significances. The model is based on the assumption that the differences between the concentrations measured using the “other” filter and Emfab may be expressed as follows:

$$d(m) = a + b \cdot \bar{m}$$

In which:

d(m) = difference between the concentrations obtained using the “other” filter and the Emfab filter;
a = constant contribution to the difference, attributable to, e.g., the influence of the filter;
b = proportional contribution to the difference, attributable to, e.g., the influence of the PM on the filter;
$\bar{m}$ = mean concentration of “other” filter and Emfab.

The variance of the mean concentration may be described as:

$$u^2(\bar{m}) = s^2(0) + r^2(\bar{m})^2$$

In which:

$u^2(\bar{m})$ = the variance of the mean concentration;
s(0) = the standard deviation of the mean at zero concentration;
r = the relative standard deviation of the mean for concentrations > zero.

The parameters a, b, s(0) and r are calculated using maximum-likelihood estimation (MLE).
The results of the calculations are given below.

Filter	Nr. data	Constant a	Proportional b	s(0)	r
Whatman GF10	198	0,52	0,032	0,42	0,046
Whatman QMAp	96	**0,32**	0,024	0,00	0,047
Whatman PTFE	93	0,24	-0,027	1,14	0,025
Pall Tissuquartz	69	0,82	-0,016	1,03	0,026
Pall Fiberfilm	52	0,20	-0,017	0,44	0,035

The results indicate that the differences are not significant, with exception of the difference at zero mean between the results of Whatman QMAp and Emfab.

Again, however, because of the relatively low concentrations no observations can be made about the comparability for higher levels of PM_{10}.

In Summary

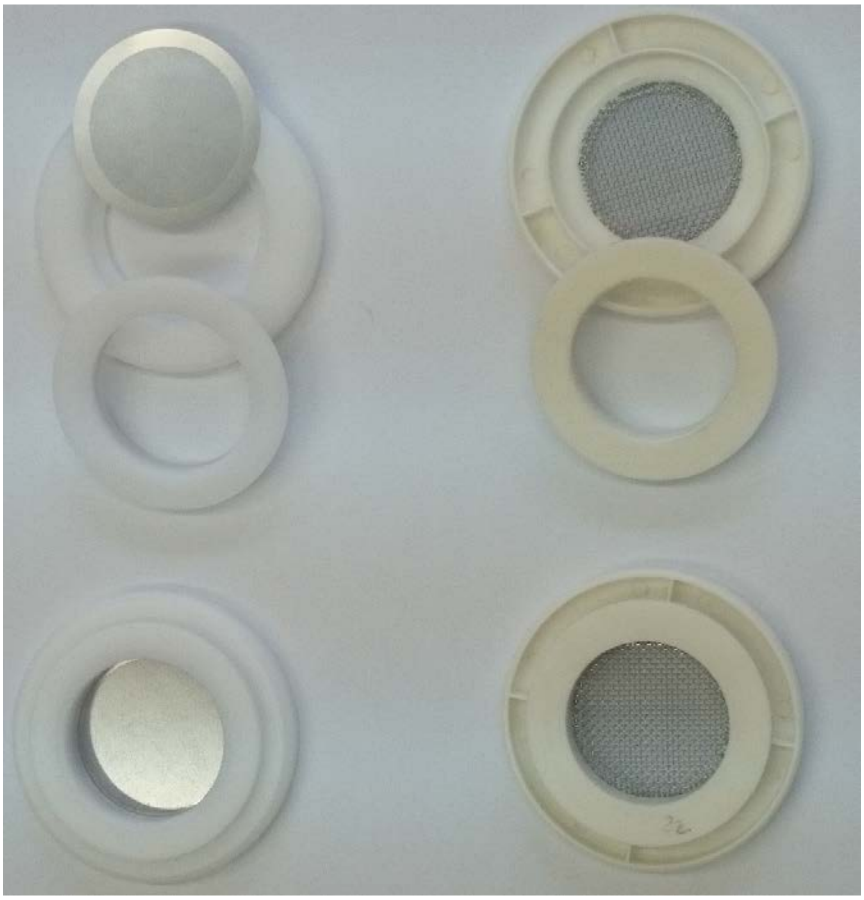
The evaluations of the results of the parallel measurements indicate that there may be some significance in the difference in behaviour of the filters due to differences in composition.

Filters that basically consist of inorganic material (Whatman GF10, Whatman QMA – preconditioned, Pall Tissuquartz QAT UP) yield higher results than the Emfab PTFE-coated glass-fibre filter. The differences may have their origins in slope (GF10) or intercept/model result (QMAp, TQ) at zero mean. PTFE and Fiberfilm filters yield results comparable to those for Emfab.

However, because of the relatively low concentrations observed it is not possible to draw any conclusions about the comparability for higher levels at which more differences may be expected due to the compositions of the filters and associated differences in sampling efficiency for PM_{10} and uptake/release of, e.g., water vapour and inorganic salts and gases.

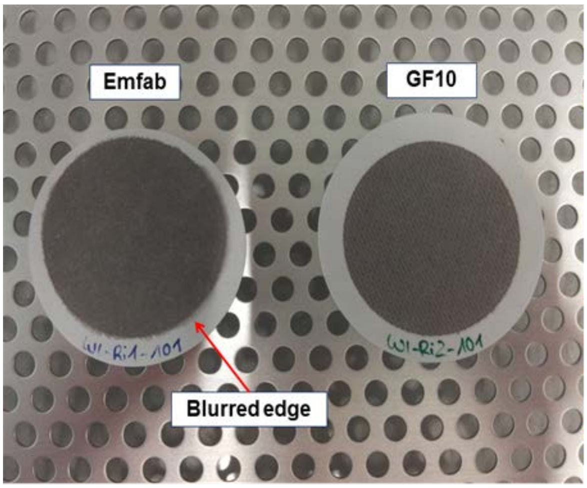
4.4.7.3 SEQ Filter Holders

Two of the four organisations used SEQ47/50 reference methods as manufactured by Sven Leckel GMBH. Sven Leckel have previously released a new kind of filter holder. The newer type of filter holders are shown on the left, and the older kind on the right in the following photograph.

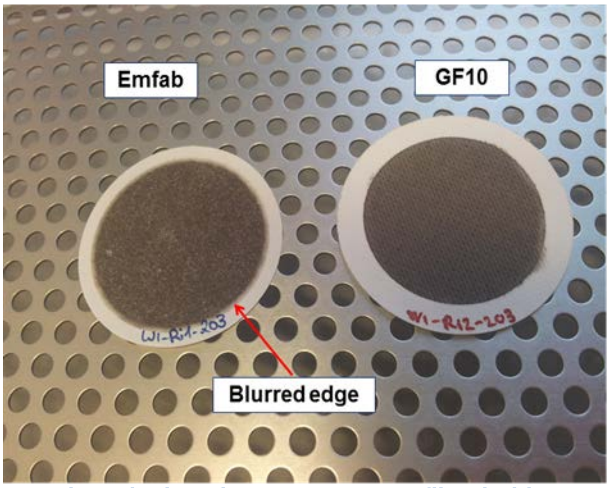


HLUG were initially using the older type, and noted the following:

“Loaded Emfab filters showed a kind of blurred edge most of the time. The edge of the sampling spot is less distinct. Due to some information that the phenomenon could be caused by an old type of filter holders, a new type of filter holders were used for sampling from the 4th November 2014. The effect occurred with an old but also with a new type of filter holders. However, no serious leaks or loss of particle mass can be claimed. Also with GF10 filters occasionally a blurred small area at the edge of the filter spot can occur. This can possibly be caused by humidity. However, the phenomenon seems not to affect the sampling efficiency and seems not to lead to lower results.



Blurred edge phenomenon, old filter holder



Blurred edge phenomenon, new filter holder

“

The statement that the blurred edge was based upon analysing different date ranges of data in accordance with the equations within CEN/TS 16450:2013, and is covered in the HLUG report in the Annex to the herein report.

Ricardo-AEA provided additional information:

“The below image is straight from the sampler, untouched. You can see that there is a clear white band on the inside edge of the filter holder that appears to have some particle encroachment

The below image is the same filter with the top half of the holder removed. The blurred halo is much more visible, but the exposed circle is complete and no further leakage beyond the sample holder is seen.

”

This supports the hypothesis that the blurred edge is not associated with particle loss, and that the filter holders supplied by Sven Leckel GMBH are appropriate for use.

4.4.7.4 Reference Method Filter Storage Parameters

An earlier draft of the reference method standard: EN12431:2014 required that the filters are stored in a controlled temperature between 19 and 21 °C after sampling. In order to verify this, the temperature of the sampled filters should be logged. Amsterdam used versions of the reference method that are modern enough to have this facility. Analysis of the data shows that the filters were retained between 19 and 21 °C throughout. This proves that the requirement to store sampled filters between 19 and 21 °C is achievable.

4.4.7.5 Weighing Room Parameters

The latest version of the reference method standard: EN12431:2014 requires that filters are weighed in an environment maintained between 19 and 21 °C and between 45 and 55 % RH. All four organisations were able to maintain their weighing room facilities within these limits. This proves that the requirement to store filters between 19 and 21 °C and between 45 and 55 % RH is achievable.

4.4.7.6 Repeat Weighing of Blanks

Before sampling, filters are weighed twice. The below table shows the difference between consecutive filter weighings of filters prior to deployment at site. These are blank filters that are not intended for sampling. There is a difference both in terms of filter media and laboratory.

Site	Filter Type	n	Min / µg	Max / µg	STDEV
Amsterdam	Conditioned QMA	6	-4	9	4,8
Amsterdam	Emfab	8	-4	7	4,4
Wiesbaden	GF10	27	-6	8	3,3
Wiesbaden	Emfab	27	-3	3	1,8
Athens	Teflon	14	-19	13	10,0
Athens	Emfab	14	-13	13	7,7
Harwell	Tissuquartz	6	10	49	15,3
Harwell	Fiberfilm	6	0	1	0,5
Harwell	Emfab	7	-2	1	1,2

After sampling, filters are again weighed twice. The below table shows the difference between consecutive filter weighings of filters after deployment at site. These are the same blank filters as above that are not intended for sampling. There is again a difference both in terms of filter media and laboratory. Tissuquartz and Teflon filters stand out as being particularly unstable.

Site	Filter Type	n	Min / µg	Max / µg	STDEV
Amsterdam	Conditioned QMA	6	-6	10	6,0
Amsterdam	Emfab	8	-2	5	3,0
Wiesbaden	GF10	27	-6	8	3,7
Wiesbaden	Emfab	27	-7	4	2,3
Athens	Teflon	14	-25	22	12,6
Athens	Emfab	14	-13	19	6,9
Harwell	Tissuquartz	6	5	40	12,8
Harwell	Fiberfilm	6	0	1	0,5
Harwell	Emfab	7	-1	1	0,6

The below table shows the average mass of both weighings after deployment at site minus the average mass of both weighings prior to deployment at site. One of the Teflon filters had lost 1 mg between the initial and final weighings. It is possible that a part of the filter had fallen off. This outlier has been removed from the below table. While it is possible to consider removal of the outlier it will be less obvious that the filter is an outlier during routine operation. Tissuquartz also stands out as being particularly unstable. Considering all four laboratories in turn, Emfab was the most stable filter media relative to the other media used. This confirms the results of the literature (Work Package 3) and laboratory (Work Package 5) studies that were used to decide on Emfab as the preferred filter media for the field studies (Work Package 2).

Site	Filter Type	n	Min / µg	Max / µg	STDEV
Amsterdam	Conditioned QMA	6	-25	19,5	15,6
Amsterdam	Emfab	8	-31	-5,5	9,0
Wiesbaden	GF10	27	-66	62	27,6
Wiesbaden	Emfab	27	-47,5	-1	11,5
Athens	Teflon	14	-43,5	48,5	29,2
Athens	Emfab	14	-3,5	25	9,2
Harwell	Tissuquartz	6	-176,5	-31	56,5
Harwell	Fiberfilm	6	-28	21,5	17,5
Harwell	Emfab	7	-11	3,5	5,2

4.4.7.7 Stability of Tissuquartz Filters

The research group at Harwell provided extra information with respect to the stability of Tissuquartz filters relative to Emfab and Fiberfilm filters. It was shown that while the comparison of Emfab and Tissuquartz filters looks good (Section 3.4.2.2 above), the stability of the weighings is not acceptable for use for mass determination purposes. A similar conclusion was drawn in Work Package 5 (Later in the herein report). The research group at Harwell note:

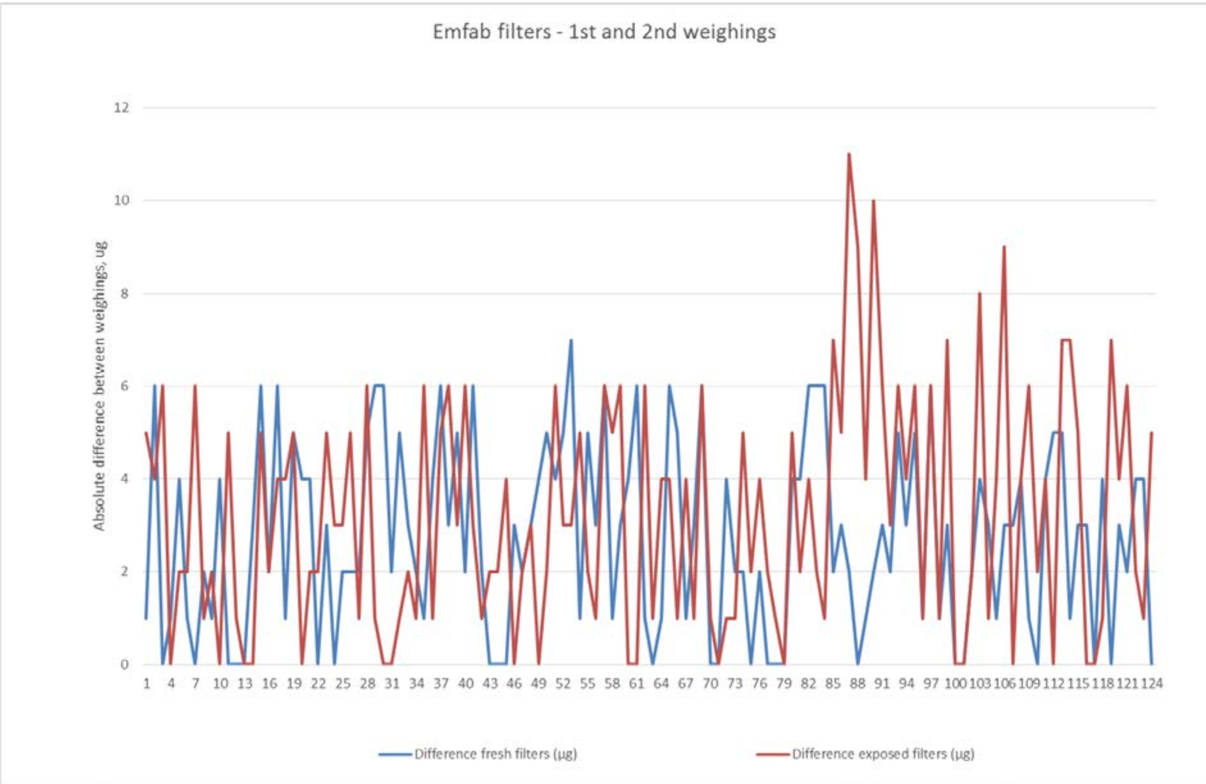
“A batch of Tissuquartz filters were weighed over an extended period from initial packet opening. This test was undertaken between June and September, before exposure of Tissuquartz filters in the sampler comparison. There was strong evidence to support mass gain of fresh filters over time, once a fresh batch of filters is opened. After 19 days of conditioning in the weighing room, the humidity control system was upgraded and humidity regulation regime was reduced from 50-52% RH, to 45-47% RH. This resulted in a net mass reduction for all filters when they were weighed on day 22, but all filters continued to gain mass after responding to this humidity change.

A selection of the results of this experiment are presented in the following table:

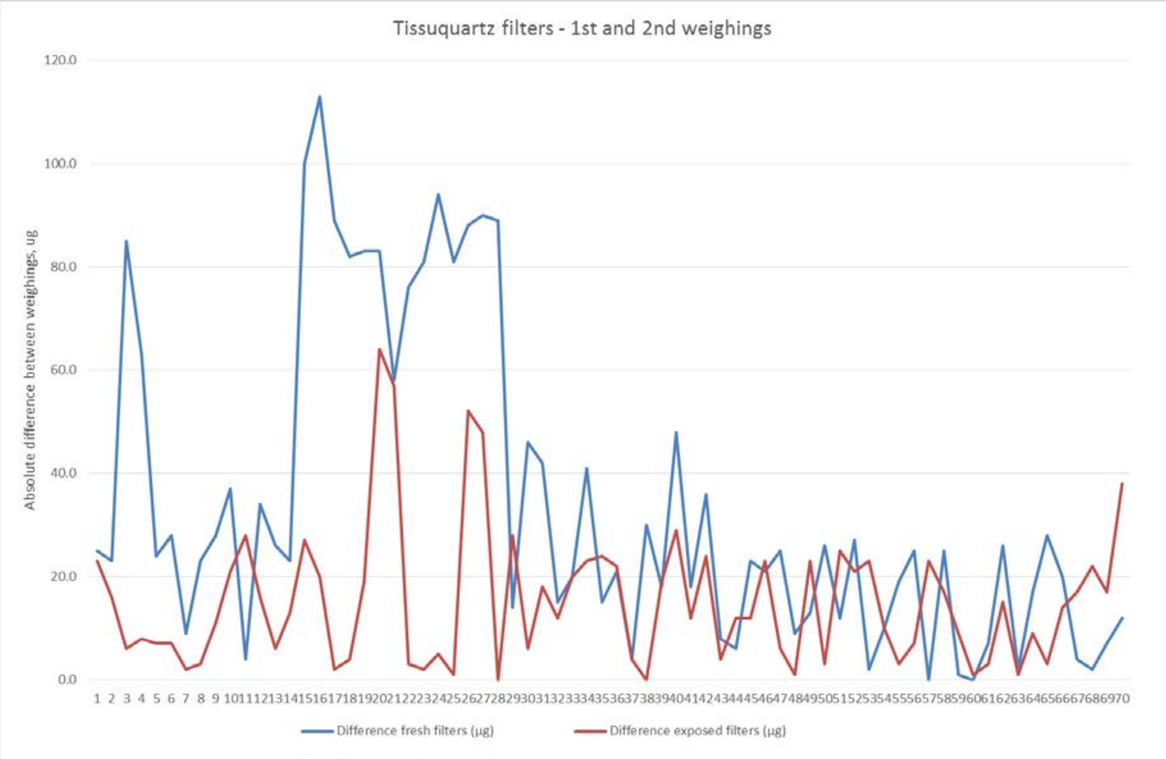
Filter Number	Mass gain, µg, Day 0	Mass gain, µg, Day 19	Mass gain, µg, Day 22	Mass gain, µg, Day 28	Mass gain, µg, Day 70
3	0	126	80	105	194
4	0	80	53	67	149
5	0	93	61	103	186
6	0	131	106	126	209
10	0	142	107	129	223
11	0	100	72	96	177
16	0	86	108	130	145

A further study was undertaken with respect to repeat weighings. The following plots shows how filter weights changed between repeat filter weighings, for both exposed and unexposed filters. The plots overlay data pre- and post- exposure, so that direct comparison of an individual filters performance can be assessed at every point along the x- axis.

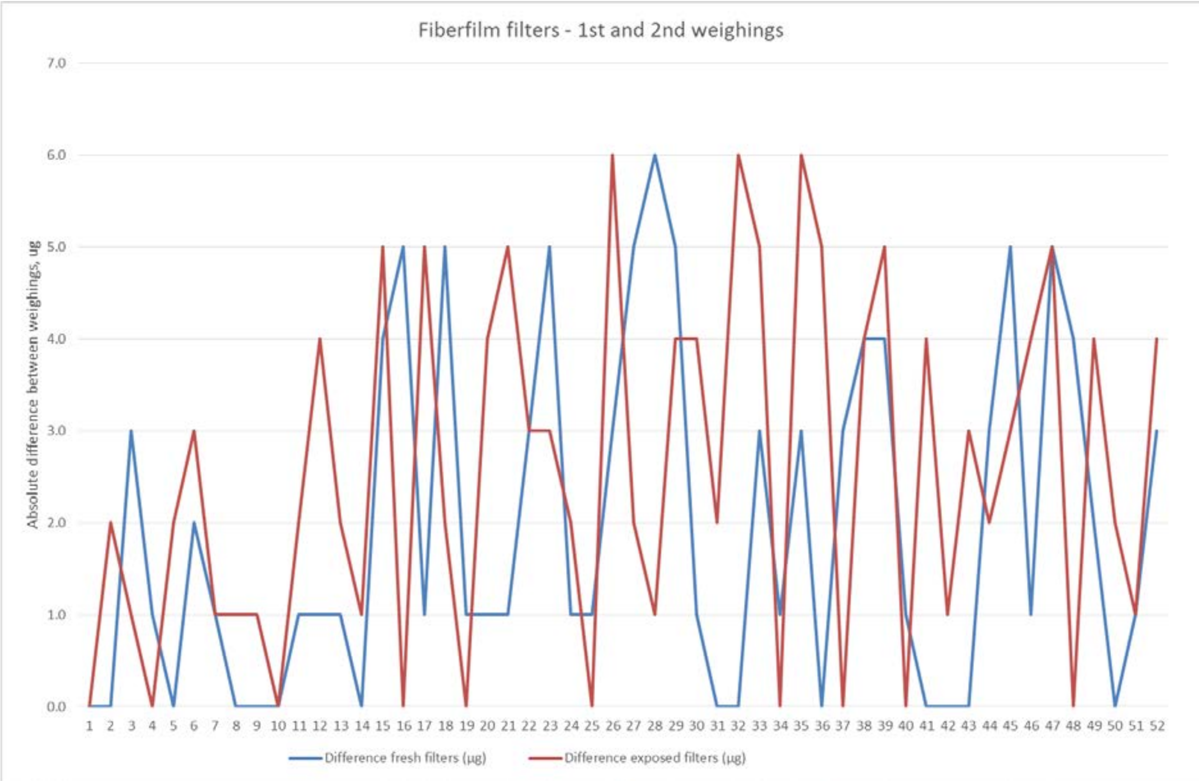
The following Figure shows the absolute difference between 1st and 2nd filter weighing for Emfab. It can be seen that Emfab filters perform well, regardless of whether the filter is loaded or fresh. The differences between weighings is well within the required limits.



The following Figure shows absolute difference between 1st and 2nd filter weighing for Tissuquartz. This plot shows that fresh Tissuquartz filters eventually settle into reasonable performance. Because of the batch weighing, the performance in batches 3, 4 and 5 are better than batches 1 and 2. The total time taken for a fresh pack of Tissuquartz filters to become conditioned (in a weighing room environment) to provide acceptable performance was in the order of 100 days. There is some initial evidence that the fresh filters gain more weight than the same filter post-exposure, but this improves to be undetectable after batch 2 has been exposed. The magnitude of the difference between weighings is at least 4 times higher for Tissuquartz than that seen for Emfab. Once the filters have settled after opening the packet (100 days in the UK test), repeat weighing performance was seen to be acceptable.



The following Figure shows the absolute difference between 1st and 2nd filter weighing for Fiberfilm. This plot shows similar performance to Emfab. There does not appear to be any significant difference between exposed and fresh filter performance, and the magnitude of the difference between repeat weighings is much better than that required by EN12341:2014.



"

4.4.7.8 Candidate Method Operational Checks

Each of the organisations were asked to perform calibration checks on their candidate instruments in line with the requirements of CEN/TS 16450:2013. These are summarised in the below table.

Checks / frequency / location	CEN/TS 16450 Section	Action Criteria	Comments
Checks of sensors for temperatures, pressure and/or humidity (every 3 months). Tests to be performed in the field.	8.4.4	± 2 °C ± 1 kPa ± 5 % RH	It was not possible to check these criteria in the field for all the candidate instruments, but where it was possible; instruments were shown to pass these criteria.
Calibration of sensors for temperatures, pressure and/or humidity (every year). Tests to be performed in the laboratory of the field.	8.4.5	± 1,5 °C ± 0,5 kPa ± 3 % RH	It was not possible to check these criteria in the field for all the candidate instruments, but where it was possible; instruments were shown to pass these criteria.
Check of the AMS flow rate(s) (every 3 months). Tests to be performed in the field.	8.4.6	± 5 %	All instruments were able to meet this criterion on at least one occasion.
Calibration of the AMS flow rate(s) (every year). Tests to be performed in the laboratory of the field.	8.4.7	± 1 %	All instruments were able to meet this criterion on at least one occasion.
Leak check of the sampling system (every year). Tests to be performed in the laboratory of the field.	8.4.8	± 2,0 %	All instruments were able to meet this criterion on at least one occasion. In the case of some instruments, it was required to follow the manufacturer's instructions instead of those in CEN/TS 16450:2013 in order to avoid damage.
Zero check of the AMS reading (every 6 months). Tests to be performed in the laboratory of the field.	8.4.9	± 3 $\mu g/m^3$	All instruments were able to meet this criterion on at least one occasion, but it was difficult to attain this criterion for some instruments that used nephelometry combined with Beta Attenuation.
Check of the AMS mass measuring system (As recommended by manufacturer and after repair, but at least every year). Tests to be performed in the laboratory of the field.	8.4.10	± 3 %	Fulfilment of this criterion was only possible where a method of calibrating the instrument was made available.

In relation to 8.4.10, within CEN/TS15450:2013 there is the following note:

“For optical AMS this calibration can only be performed by comparison with the reference method or with an appropriate reference standard”.

This note is retained in the text of the new standard.

Based on the findings of Work Package 2, the text of the new standard has been modified to add a note to sections 8.4.4 and 8.4.5:

“For some instruments such checks and calibrations are not possible *in situ* because of the positioning of the sensors within the AMS. In these cases checks may be performed in a laboratory room with constant temperature and relative humidity by comparing sensor readings (after stabilisation) with those of reference standards”.

In relation to leak checks (Section 8.4.8), both CEN/TS 16450:2013 and the new standard refer the user to Section 7.4.6, where the requirement for leak checks is discussed as part of the laboratory test procedures. CEN/TS 16450:2013 is very proscriptive with regards to the test procedures to be used. Based on the findings of Work Package 2, the text of the new standard has been modified to be more pragmatic:

“The leak tightness (leak rate) of the complete flow path of the AMS (sample inlet, sampling line, measuring system) shall be tested according to the manufacturer´s specification. A leak test integrated in an AMS can be used, provided that the stringency of such a test is suitable for a proper assessment of the instrument´s tightness. If the complete system cannot be tested for technical reasons, the leak rate can be determined separately for each element of the flow path. In case proper sealing of the sample inlet is impossible, the inlet may be excluded from the test. This test may require the use of either a pressure measuring device, or a volumetric flow meter.”

Based upon the leak test results obtained by the Wiesbaden group, the leak test criterion was changed from 2,0% to 2 %.

In 8.4.5 and 8.4.7, the action criteria have been renamed “Uncertainty requirements for transfer standards”.

As some instruments could fail the criteria when functioning within their normal operating parameters, the Sections on zero, leak and flow rate tests have been modified to require that if the criterion is exceeded, then ’ the user shall take any action it judges to be appropriate for the specific situation’.

An extra Section has been added with recommendations on how the user can correct the data if any of the criteria are exceeded.

4.4.7.9 Candidate Method Equivalence Calculations

The mathematics used in CEN/TS 16450:2013 was first published in Guide to Demonstration of Equivalence 2010, and remains unchanged in CEN/TS 16450:2013. All four organisations followed the equivalence calculations set out in CEN/TS 16450:2013. All four organisations used the official spreadsheet as posted on the Europa website in order to make these calculations. These calculations are too numerous to be repeated herein, and can be observed in the individual reports in the Annex. The equations were shown to be very effective in indicating the equivalence of candidate methods with respect to the reference method, and it was not necessary to make any changes in the text of the revised standard.

Within the new standard, additional equations were added in order to split the uncertainty in to ‘Bias at the Limit Value’ and ‘Random Uncertainty’. These calculations are very useful for Member States when interpreting PM_{10} and $PM_{2.5}$ measurements for submission to the European Commission.

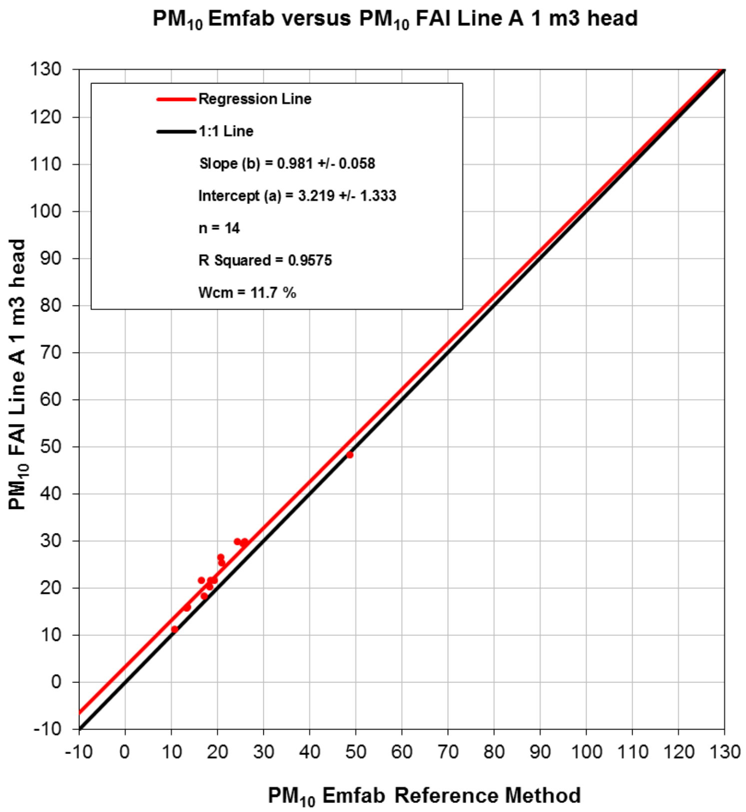
4.4.7.10 Coarse PM at the Industrial Site

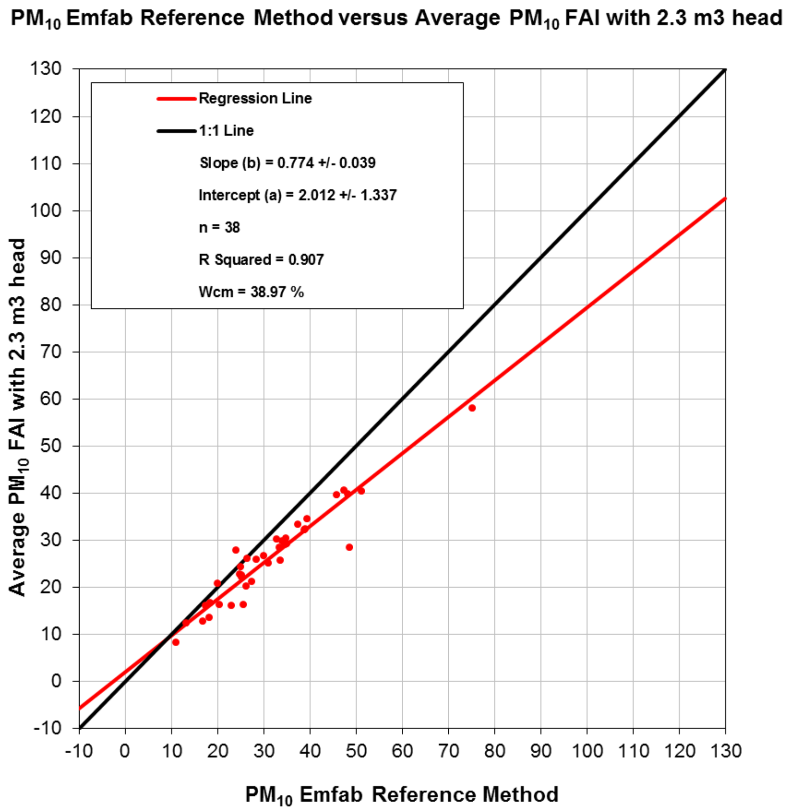
The Amsterdam site has a steel works to the east, sea to the west, and sand dunes surrounding the site. All three of these are known to produce coarse particles. As such the site is very challenging for PM_{10} monitoring instruments. At the site there was:

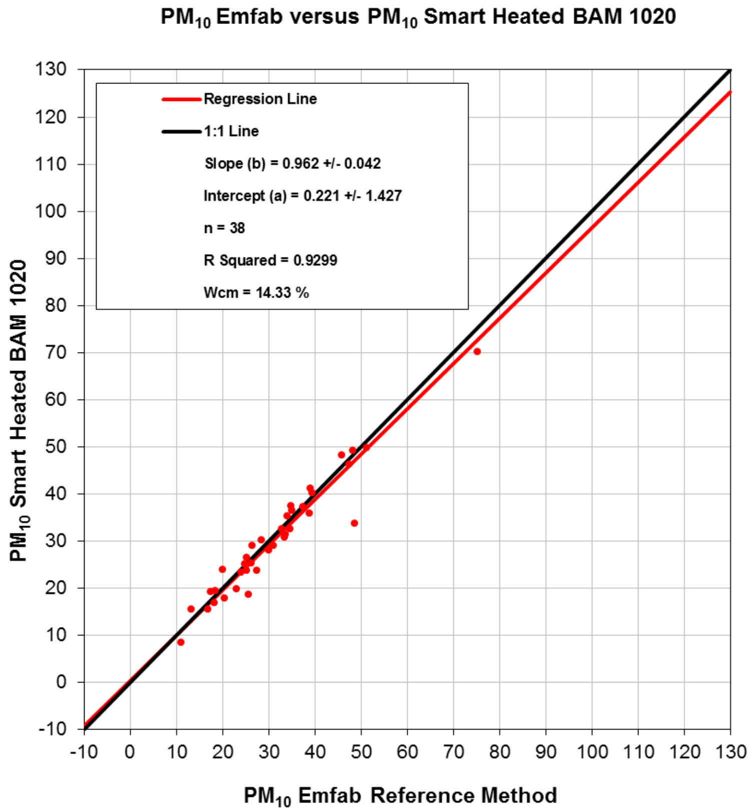
- A FAI SWAM Dual Channel Instrument operated in hourly filter change mode. This instrument has two parallel channels, and can operate with PM_{10} and/or $PM_{2.5}$ heads at either 1 or 2,3 m^3hr^{-1}. In both the UK and Germany, the instrument has been equivalence tested while operating at 2,3 m^3hr^{-1}. It has been proven equivalent to the PM_{10} and $PM_{2.5}$ Reference Methods. In both cases, there was no requirement need for slope and/or intercept correction. However; at a gravel pit test site in Germany, the instrument was shown to overestimate the PM_{10} Reference Method. The FAI instrument was operated with heads that complied with the drawings in the then PM_{10} Standard: EN12341:1998. Conversely, the reference method heads were built to a different design with a sharper cut characteristic. The overestimation was due to there being many particles close to 10 microns in diameter that were sampled by the FAI head, but not by the Reference Method Inlet. The revised PM_{10} Standard: EN12341:2014 adopted the inlet design with the sharper cut characteristics, but allowance was made for the 1998 design inlets in an Annex. At the Amsterdam test site, the FAI was operated with 2,3 m^3hr^{-1} heads of the older 1998 design, whereas the reference method was operated of the 2014 design. At the Amsterdam Test Site, the FAI was also operated with 1 m^3hr^{-1} heads that are designed to be similar to the 2014 style inlets but to maintain the same cut characteristics for a lower flow rate.
- A PM_{10} Smart Heated BAM 1020 operated with an EU style 1 m^3hr^{-1} head. In The Netherlands, this has been shown to be equivalent to the PM_{10} Reference Method when operated with preconditioned Whatman QMA Quartz filters and with EN12341:2014 style heads.
- $PM_{2.5}$ Smart Heated BAM 1020 operated with a US style 1 m^3hr^{-1} head, followed by a Very Sharp Cut $PM_{2.5}$ Cyclone (VSCC). In The Netherlands, this has been shown to be equivalent to the $PM_{2.5}$ Reference Method when operated with preconditioned Whatman QMA Quartz filters.

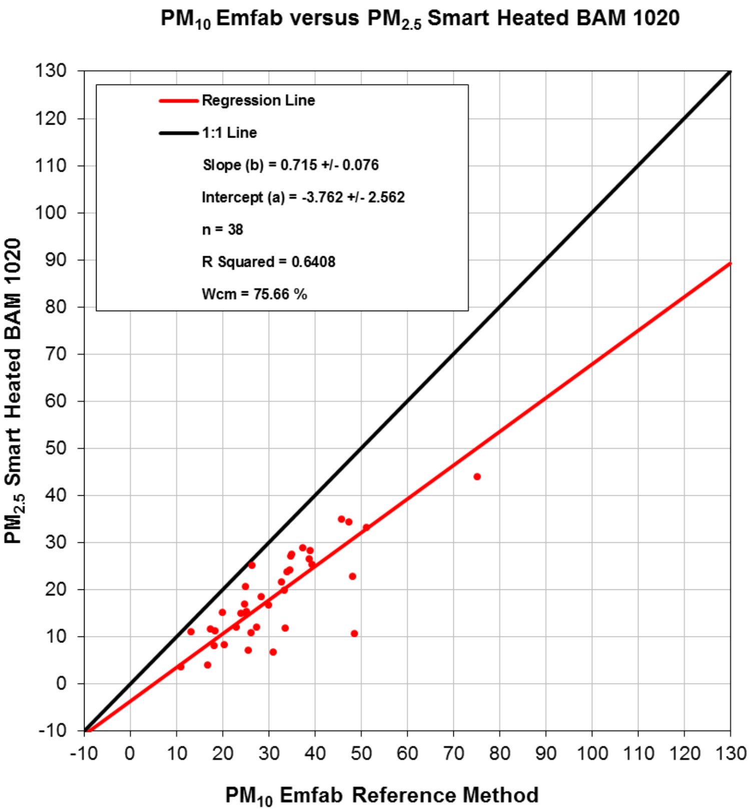
Overleaf are four graphs showing the equivalence calculations upon 24 hour averages of the candidate method's data. These graphs show in turn that:

1. When operated with 1 m^3hr^{-1} European style heads, the FAI SWAM agrees with the reference method that is operated with EN12341:2014 style heads and with Emfab filters;
2. When operated with 2,3 m^3hr^{-1} EN12341:1998 heads, the FAI SWAM underestimates the reference method that is operated with EN12341:2014 style heads and with Emfab filters;
3. The PM_{10} Smart Heated BAM generally agrees the reference method that is operated with EN12341:2014 style heads and with Emfab filters. There is one data point for which the BAM significantly underestimates the reference method.
4. The $PM_{2.5}$ Smart Heated BAM heavily underestimates the reference method that is operated with EN12341:2014 style heads and with Emfab filters. The level of the underestimation indicates that there is a very high level of coarse particles at the Amsterdam site.


PM10 Emfab versus PM10 FAI Line A 1 m3 head
Regression Line
1:1 Line
Slope (b) = 0.981 +/- 0.058
Intercept (a) = 3.219 +/- 1.333
n = 14
R Squared = 0.9575
Wcm = 11.7 %
PM10 FAI Line A 1 m3 head
PM10 Emfab Reference Method
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130

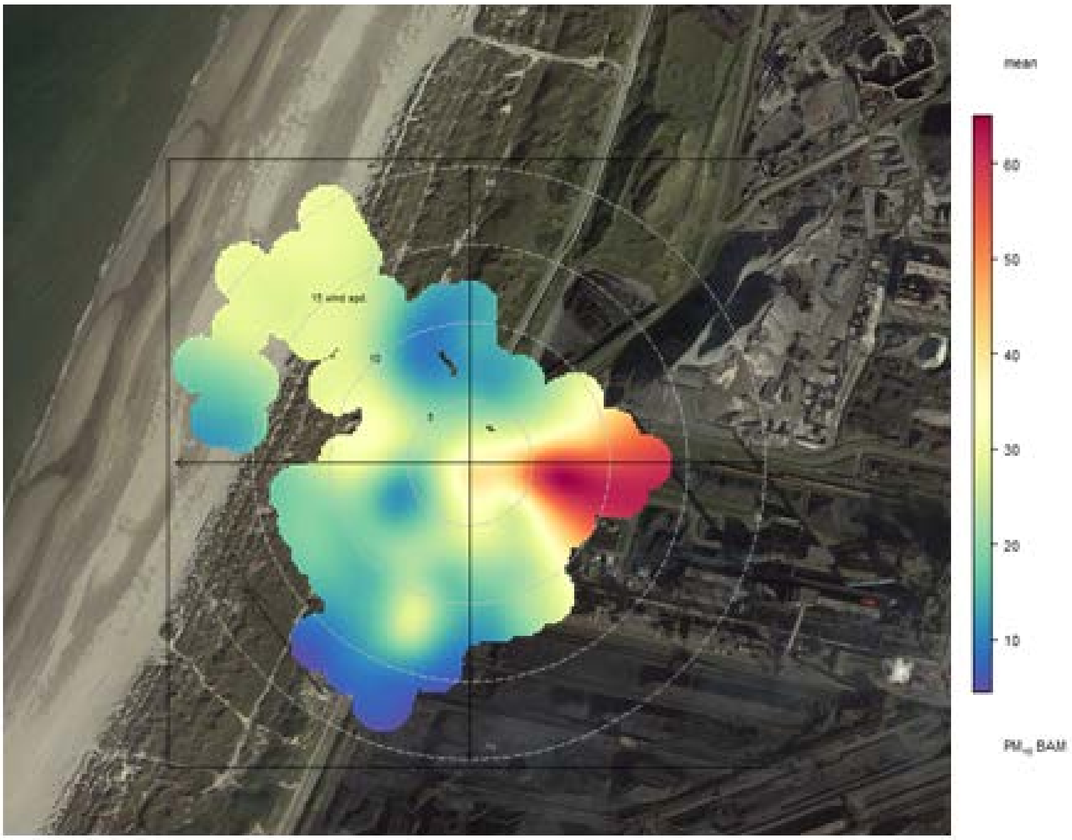

PM10 Emfab Reference Method versus Average PM10 FAI with 2.3 m3 head
Regression Line
1:1 Line
Slope (b) = 0.774 +/- 0.039
Intercept (a) = 2.012 +/- 1.337
n = 38
R Squared = 0.907
Wcm = 38.97 %
Average PM10 FAI with 2.3 m3 head
PM10 Emfab Reference Method
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130

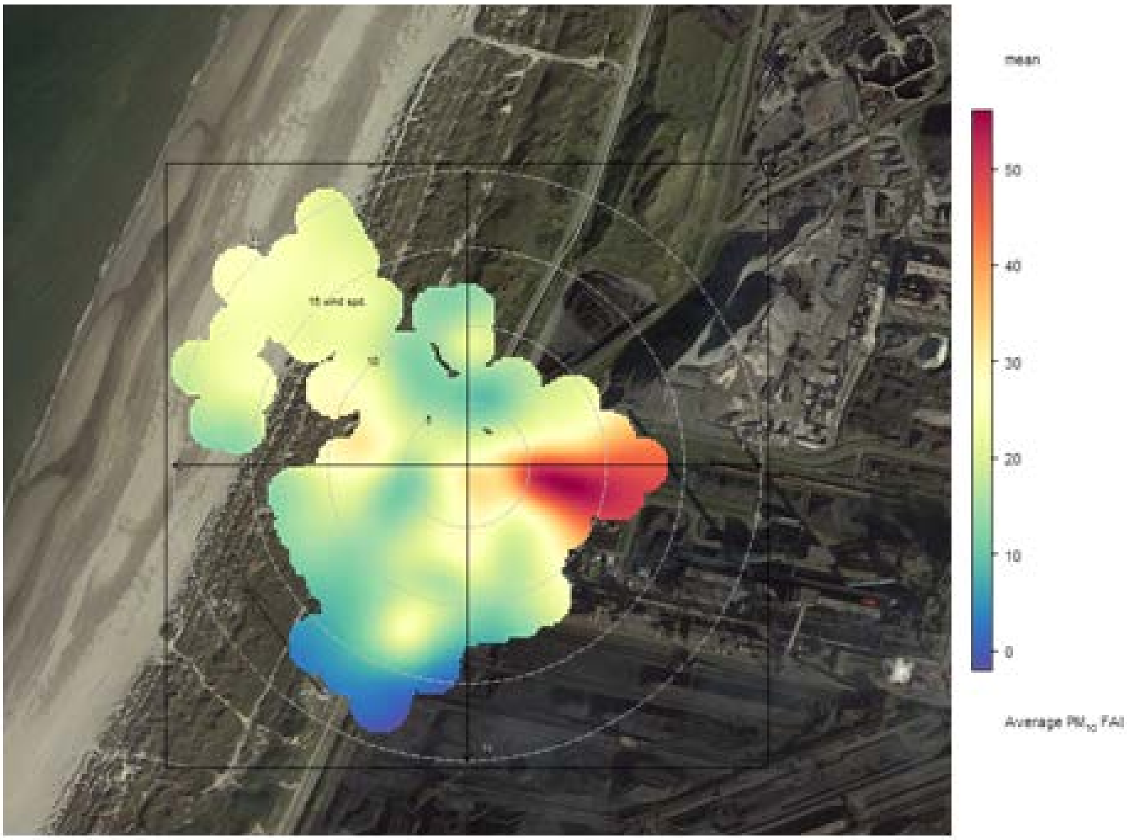

PM10 Emfab versus PM10 Smart Heated BAM 1020
Regression Line
1:1 Line
Slope (b) = 0.962 +/- 0.042
Intercept (a) = 0.221 +/- 1.427
n = 38
R Squared = 0.9299
Wcm = 14.33 %
PM10 Smart Heated BAM 1020
PM10 Emfab Reference Method

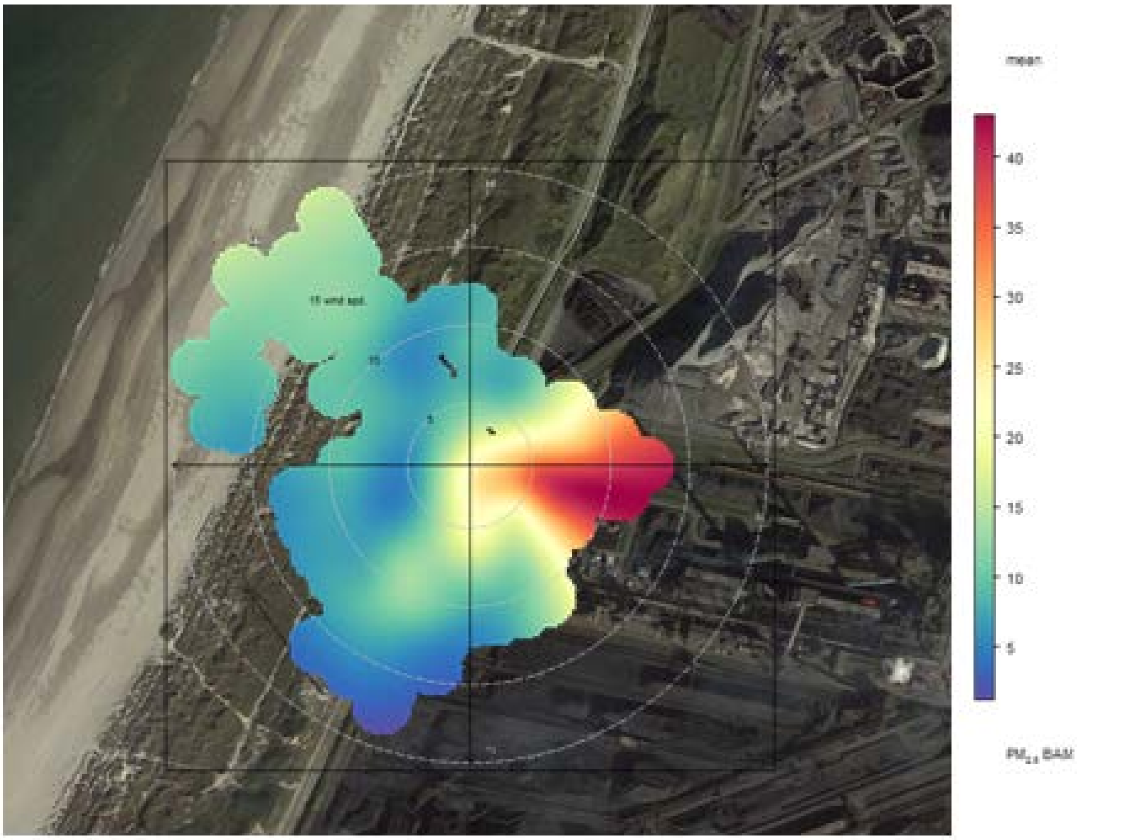

PM10 Emfab versus PM2.5 Smart Heated BAM 1020
Regression Line
1:1 Line
Slope (b) = 0.715 +/- 0.076
Intercept (a) = -3.762 +/- 2.562
n = 38
R Squared = 0.6408
Wcm = 75.66 %
PM2.5 Smart Heated BAM 1020
PM10 Emfab Reference Method

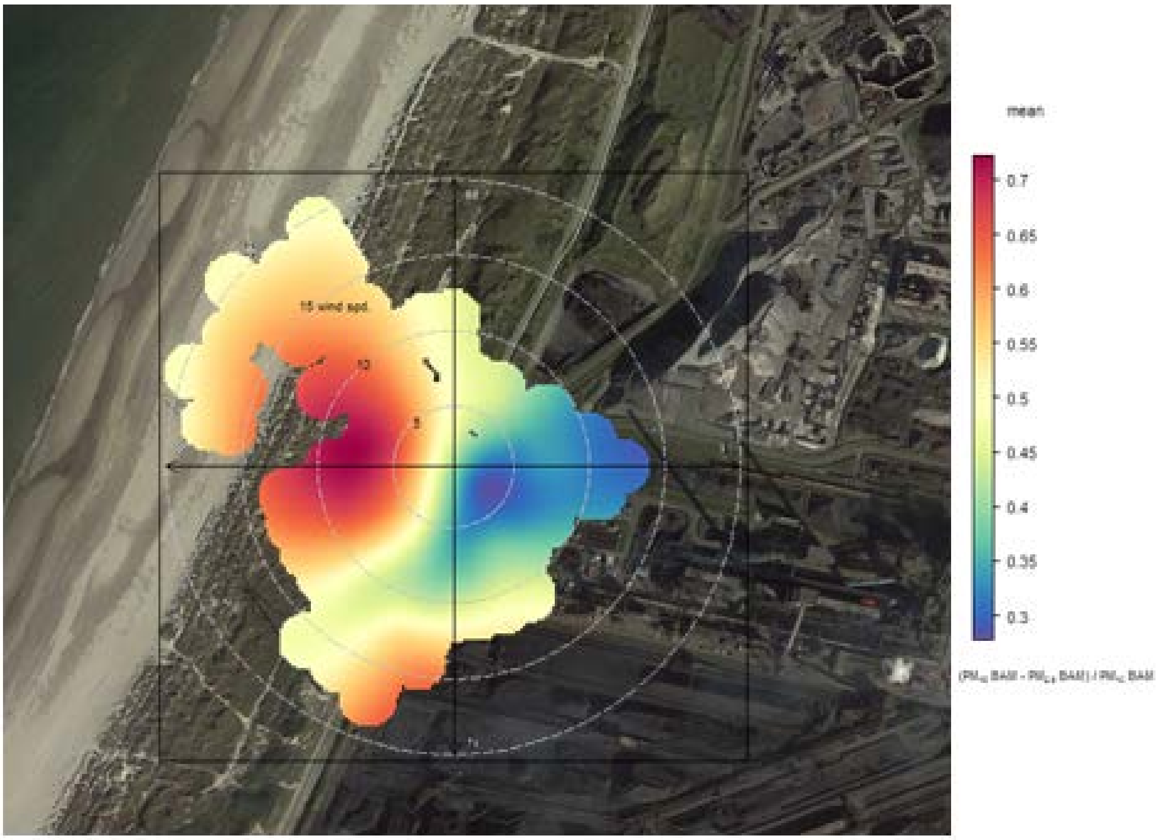
Below and overleaf are five diagrams. These diagrams were drawn using openair software operating under the R statistical package (www.openair-project.org). They show polar plots that combine wind direction and wind speed with average pollutant levels. Red shading indicates the direction from which the highest concentrations originate. The polar plots are overlaid upon Google Earth imagery. These diagrams were drawn using hourly data as measured by the candidate instruments. As the reference methods only operate using 24 hour samples, it is not possible to include them on the diagram. In turn the five diagrams indicate that:

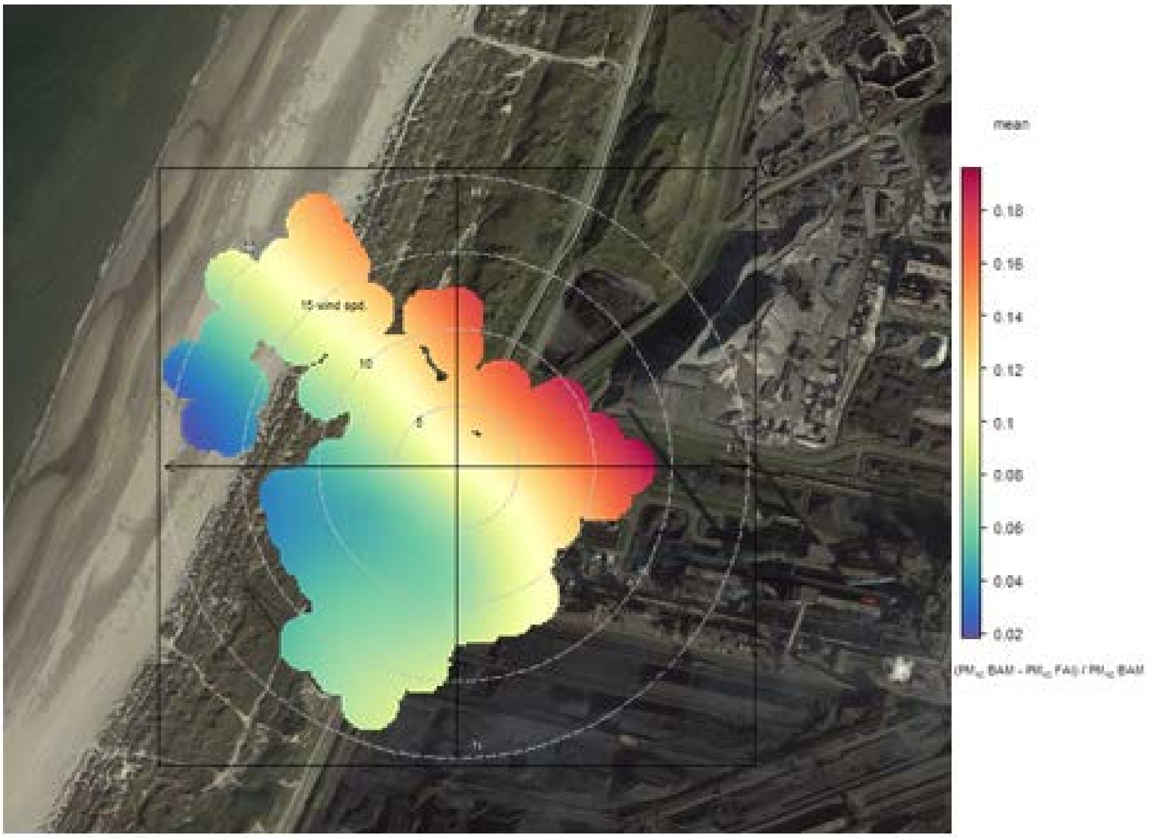
1. The PM_{10} Smart Heated BAM displays the highest concentrations when the air mass has passed over the steelworks;
2. For the period when both inlets of the FAI were operated with EN123431:1998 style heads, the concentration was averaged. The instrument displays the highest concentrations when the air mass has passed over the steelworks;
3. The $PM_{2,5}$ Smart Heated BAM also displays the highest concentrations when the air mass has passed over the steelworks which indicates that the steel works are the primary source of both PM_{10} and $PM_{2.5}$ in the area;
4. The relative coarse fraction as measured by the BAMs was calculated as (PM_{10} BAM - $PM_{2,5}$ BAM) / PM_{10} BAM. This shows that when the air mass has originated from the sea, the highest proportional impact upon coarse particle concentrations is observed, even though in absolute terms the PM levels are comparatively low.
5. The relative underestimation of the PM_{10} FAI to the PM_{10} BAM was calculated as (PM_{10} BAM – PM_{10} FAI) / PM_{10} BAM. The pattern of this diagram is notably different to that of the relative coarse fraction as measured by the BAMs (above). This diagram instead shows that in relative terms, the underestimation of the PM_{10} FAI to the PM_{10} BAM is most significant when the air mass has passed over the steel works. This evidence suggests that the coarse material generated by the steel works is responsible for the underestimation of the PM_{10} FAI operated with 2,3 m^3hr^{-1} EN12341:1998 heads.




15 wind spd.
10
5
mean
50
40
30
20
10
0
Average PM10 FAI


15 wind spd.
10
5
mean
40
35
30
25
20
15
10
5
PM2.5 BAM


mean
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
(PM_{10} BAM - $PM_{2.5}$ BAM) / PM_{10} BAM
15 wind spd.
10
5


mean
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
(PM_{10} BAM - PM_{10} FAI) / PM_{10} BAM
15 wind spd.
10
5

It is noted that at the gravel site in Germany, that the PM_{10} FAI operated with 2,3 m^3hr^{-1} EN12341:1998 heads overestimated the PM_{10} Reference method operated with 2,3 m^3hr^{-1} EN12341:2014 heads. Whereas at the Amsterdam site, the PM_{10} FAI operated with 2,3 m^3hr^{-1} EN12341:1998 heads instead underestimated the PM_{10} Reference method operated with 2,3 m^3hr^{-1} EN12341:2014 heads. Both the 1998 and 2014 design heads have the same cut point of 10 microns at 50 % efficiency, but the cut characteristics of the 1998 head are less sharp. This evidence suggests that at the German site there were many particles slightly greater than 10 microns in diameter, whereas at the Amsterdam site, there were many particles slightly lower than 10 microns in diameter.

In summary, this study provides further evidence that in industrial locations, that reference method and candidate instruments should be operated with PM_{10} heads corresponding to the design published in EN12341:2014, and not those corresponding to the design published in EN12341:1998.

5. Contract item 2012-11.1.1 – "Automated Measuring Systems for Particulate Matter"

1/	**Identification**	• WI number 00264162, EN XXXXX • Contract item SA/CEN/ENTR/503/2012-11 • covers item 1 of mandate M/503
2/	**Title**	Automated Measuring Systems for Particulate Matter
3/	**Progress of work**	present stage : Stage code 20.60 Circulation of 1st Working Draft next stage : Stage code 30.99 Dispatch Enquiry draft to CCMC
4/	**Milestones so far**	Validation work: • WP1: AMS lab tests: Two organisations were awarded sub packages. The final reports have been submitted for each organisation, and are included in the Annex herein. • WP2: Field tests: Four organisations were awarded sub packages. The final reports have been submitted for each organisation, and are included in the Annex herein. • WP3: Literature review: The final report has been submitted, and is included in the Annex herein. • WP4: Testing reversibility of water vapour: The final report has been submitted, and is included in the Annex herein. • WP5: Humidity tests: The final report has been submitted, and is included in the Annex herein. • WP6: Statistical evaluation: The herein report forms the key deliverable of this Work Package. • Project Coordinator: The standard has been drafted and submitted for CEN enquiry.
5/	**Next steps and remaining work**	A summary of remaining key steps in anticipated date order are: • July 2015: Submission of third set of invoices. • September 2016: Stage Code 49 Document available for Formal Vote • July 2017: Stage Code 64 Document published • July 2017: Submission of final invoices. TC264 WG15 will remain active throughout this period.
6/	**Documents**	Annex A of this report contains the final deliverable reports for WP1 through WP5. The herein report forms the key deliverable for WP6.

Annex A- Report Work Package 1 (sub package 1)

Annex B - Report Work Package 1 (sub package 2)

Annex C - Report Work Package 2 (traffic site)

Annex D - Report Work Package 2 (industrial site)

Annex E - Report Work Package 2 (urban background site)

Annex F - Report Work Package 2 (rural background site)

Annex G - Report Work Package 3

Annex H - Report Work Package 4

Annex I - Report Work Package 5