EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN/TC 264/WG 25 „Standard method for the determination of total gaseous mercury in ambient air“

Final Report of the WG 25
Minimum Validation Programme
Description and Results

Rende, February 2008

Contract SA/CEN/ENV/000/2005-37

Content

Part A

Summary

The European Commission (EC) is acting to reduce human and environmental exposure to a variety of air pollutants across Europe. Because of mercury's combined qualities of toxicity, environmental persistence, and potential for bioaccumulation, this metal is a particularly insidious, and an important pollutant to monitor and manage. However, sampling and analysis of mercury is not always a simple matter, and it is important to understand the key measurement issues to appropriately collect and interpret data. The application of non-validated sampling and analytical methods could lead to significant biases in measurement results. European Union policy on air quality aims to develop standard methods for the assessment of air quality and adopt these as reference methods in support of European legislation, if appropriate. Following the requirements of the Fourth Daughter Directive, Member States have to measure the TGM in the ambient air and the total deposition of mercury. Therefore, there is a strong need to develop fully validated and traceable European standard methods that will ensure the representativeness, comparability, traceability and accuracy of data produced by all Member States for mercury measurements.

Although there are different automated and manual techniques available for the measurement of TGM concentrations in ambient air, there is no standardised method available which is sufficient to meet overall objectives and requirements of the Fourth Daughter Directive. At this stage only the European standard method for the determination of the mercury concentration in water samples (EN 13506) is available but no standard method exists for the determination of mercury in precipitation (although OSPAR/EMEP reference methods are currently available for mercury in precipitation).

The Fourth Daughter Directive requires the standardised method for the measurement of TGM concentrations in ambient air to be an automated method based on atomic absorption spectrometry or atomic fluorescence spectrometry. Within the framework of the EU/EFTA mandate M/360 “Standardisation mandate to CEN for standard measuring methods for the determination of total gaseous mercury in ambient air and the total deposition of mercury”, CEN/TC 264/WG 25 was entrusted to establish a standard measurement method for the determination of total gaseous mercury (TGM) in ambient air according to the Community Directive 96/62/EC and the Council Directive 1999/30/EC. Field trials were planned and

executed by CEN/TC 264/WG 25 ‘Mercury’ in order to test and validate the proposed measurement methodologies and to ensure that they met the data quality requirements of the Fourth Daughter Directive, in particular the uncertainty requirements.

For the validation of the recommended standard method WG 25 indeed agreed on the Minimum Validation programme (MVP), which is financed by the European Commission (EC) DG Environment/NEN/CEN/CMC/DIN under Contract N. SA/CEN/ENV/000/2005-37.

The WG 25 MVP consists on laboratory tests, preparation of field tests and field tests with sampling performed for 2 months at each site over a period of 12 months at four European measurement sites (2 coastal/background and 2 local/industrial). The working range of a standardised method should, in fact, cover ambient air concentrations at background sites (coastal/rural) and at local/industrial sites in order to establish technical procedures that provide results of quality over a wide range of application (concentration levels for which the methods apply). The individual steps of the MVP, including sample pre-treatment, sampling inlet conditioning, sampling and analysis, were performed on the basis of Guidance documents (N 16 Guidance doc field tests TGM.doc), which were prepared by the Project Team (PT) of WG 25.

TGM sampling took place at four sampling sites with distinct characteristics in different seasons and thus under different meteorological conditions during late 2006 and 2007. The sites were chosen in order to get as much information as possible on the performance of the reference method in different ambient conditions. The TGM field trials have been carried out for two months at each site over a period of 12 months. The laboratories who participated in the WG 25 MVP are listed in **Table 1**, which also reports information concerning TGM field trial location, sites criteria, coordinates and sampling periods.

Table 1. Laboratories participating in the WG 25 - MVP

LABORATORY	MERCURY SITES	SITE CRITERIA	COORDINATES	CODE	PARTICIPATION IN (*)	SAMPLING PERIOD
TGM						
ITALY - CNR-Institute for Atmospheric Pollution, Rende	Southern European Remote/Background	EMEP Type/ Coastal	39.316°N 16.033°E	Lab A	LT; PFT; FT	November 2006 – January 2007
SPAIN - Instituto de Salud Carlos III, Madrid	Central/Southern European Local/Industrial	e.g. near chlor-alkaly plant	37.266° N, 6.950° W	Lab B	LT; PFT; FT	February 2007 – May 2007
SWEDEN - IVL Swedish Environmental Research Institute, Göteborg	Central/Northern European Remote/Background	EMEP Type/Inland	57.394°N, 11.914°E	Lab C	LT; PFT; FT	June 2007 – August 2007
BELGIUM - VMM Vlaamse Milieumaatschappij, Antwerp	Central/Northern European Local/Industrial	e.g. near chlor-alkaly plant	51.063°N, 5.094 °E	Lab D	LT; PFT; FT	September 2007 – December 2007

(*) LT Laboratory Tests; FT Field Tests

PFT Preparation of the Field Tests; A Analysis

The task of the MVP is to validate the standard method described in the EN of WG 25 and by this to show its suitability for the determination of TGM in ambient air to meet the requirements fixed in the 4th Daughter Directive of the EU Framework Directive. For this purpose a comprehensive statistical evaluation of the MVP results was performed and the Expanded Uncertainty, the Repeatability and the Reproducibility of the standard method were determined.

The instruments which took part at the field trials are:

- Two **Tekran** analysers
- Two **Mercury instruments** analysers
- Two **Lumex** analysers
- Two **PSA** analysers

In particular, the number of instruments at each field trial location along with the length of each study are reported below:

- **Italy:** 8 instruments, 64 days
- **Spain:** 7 instruments, 79 days
- **Sweden:** 8 instruments, 57 days
- **Belgium:** 8 instruments, 63 days

All automated instruments shall run at the same time in the same place. The principles of operation of automatic analysers are indicated in **Table 2** and the analysers parameters are reported in **Table 3**:

Table 2: Principles of analytical methods used in the analysers during the field trials.

INSTRUMENTS	COLD VAPOUR ATOMIC ABSORPTION SPECTROMETRY (CVAAS)	COLD VAPOUR ATOMIC FLUORESCENCE SPECTROMETRY (CVAFS)	ZEEMAN (AAS)
TEKRAN 2537A		X	
LUMEX RA-915+			X
MERCURY INSTRUMENTS	X		
PSA S.GALAHAD		X	

Table 3: Analysers parameters.

PARAMETERS	ANALYSERS			
	Tekran 2537 A	UT-3000	LUMEX	PSA, S. Galahad II
Date / Time	x	x	x	x
Instrument no	x	x	x	x
Channel				x
Correction factor	x			x
Signal (baseline + peak height)	x			x
Peak height	x			x
Peak area	x			x
Concentration	x	x	x	x
Slope	x	x		x
Intercept	x	x		x
Correlation coefficient	x	x		x
Baseline	x	x	x	x
Instrument status	x	x	x	x
Method name / no	x			x
Measurement mode				x
MFC (293 K, 1 atm)	x	x		x
Volume	x	x		x
Unit	x	x	x	x
Mass	x			x

The analytical conditions were performed according to the documents CEN/TC 264/WG 25 N 900 and CEN/TC 264/WG 25 N16. More details regarding the Instrumental settings and Maintenances procedure fixed by the WG 25 along with calibration and gold-traps procedures are reported in the document CEN/TC 264/WG 25 N 16 and related Annexes. Some changes from these documents and/or additional maintenance made during the field trials are documented specifically in the Annexes of this document reporting the field tests performance at each site and the measurements narratives as well.

The daily averages measured at each site are detailed in the figures below.

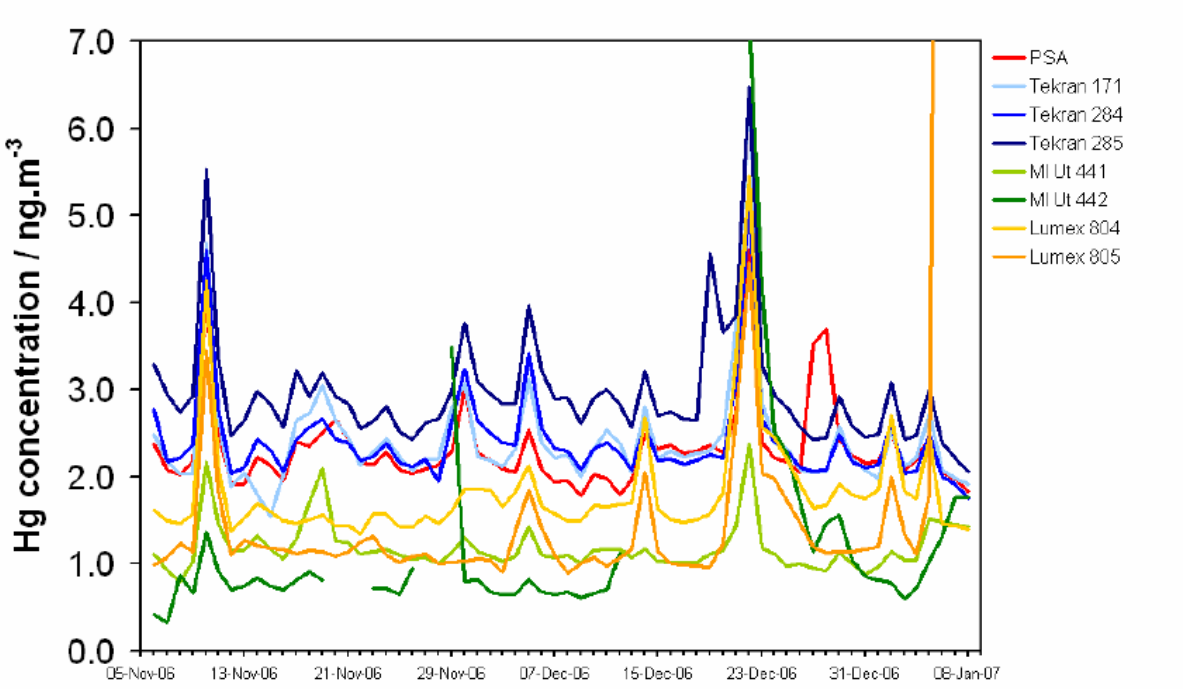

Figure 1. Daily mass concentration data from the Italian TGM field trial.

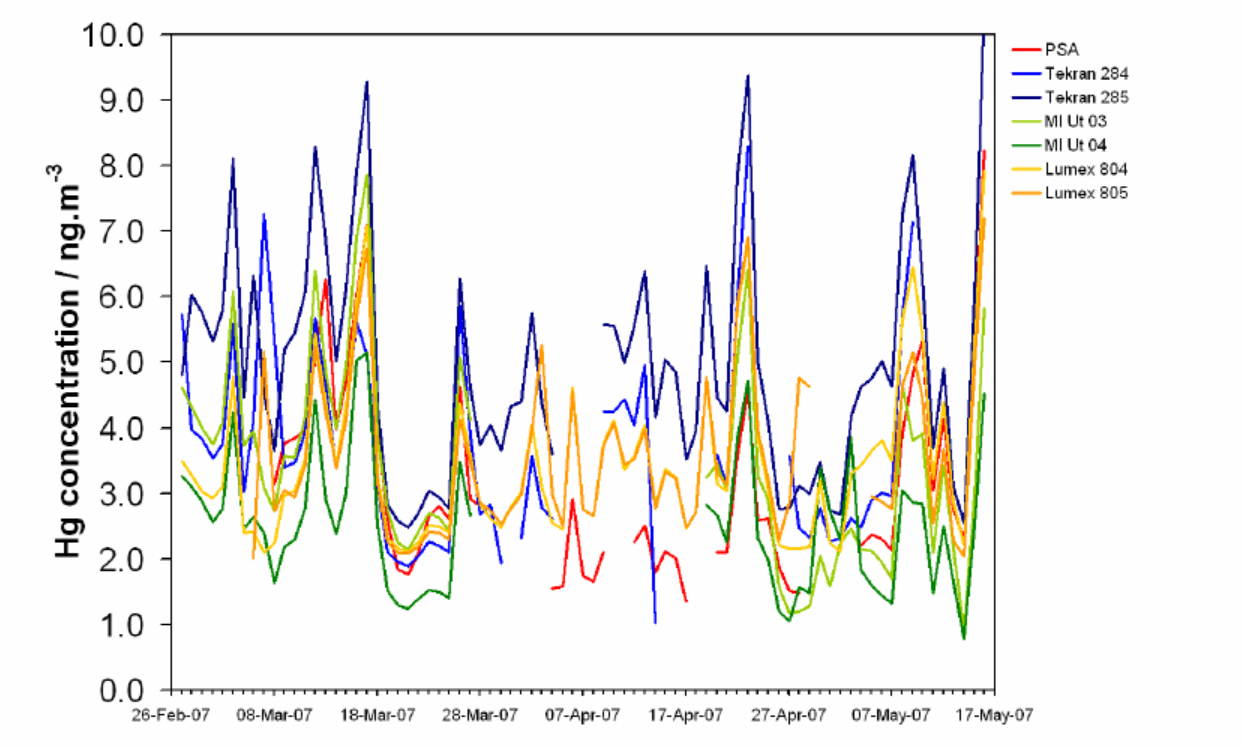

Figure 2. Daily mass concentration data from the Spanish TGM field trial.

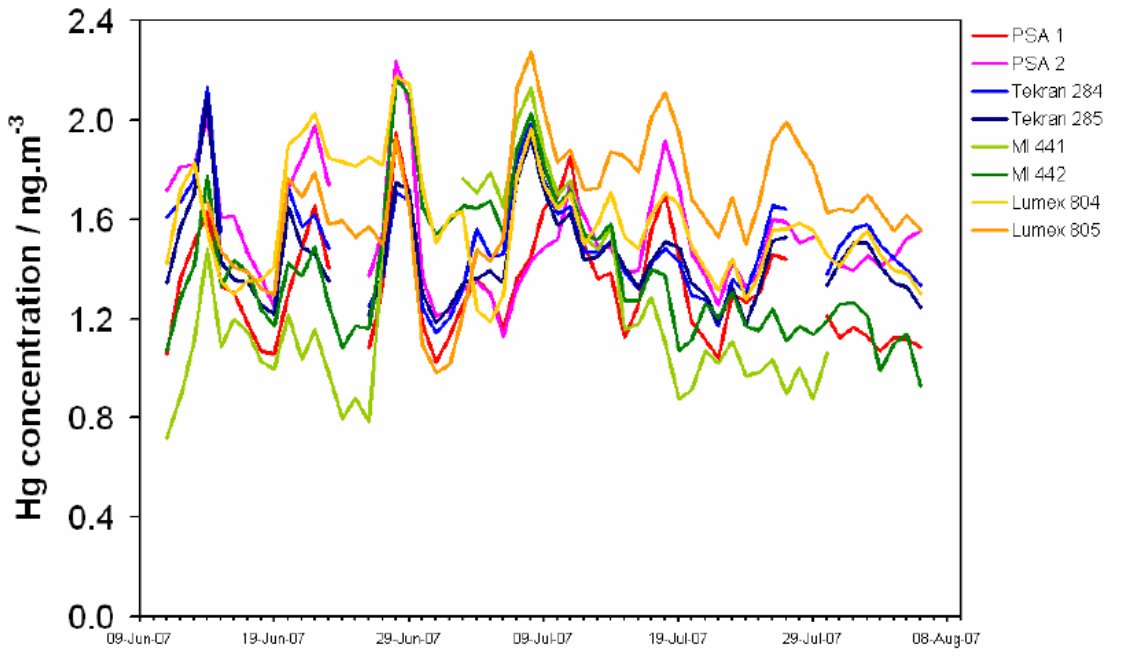

Figure 3. Daily mass concentration data from the Swedish TGM field trial.

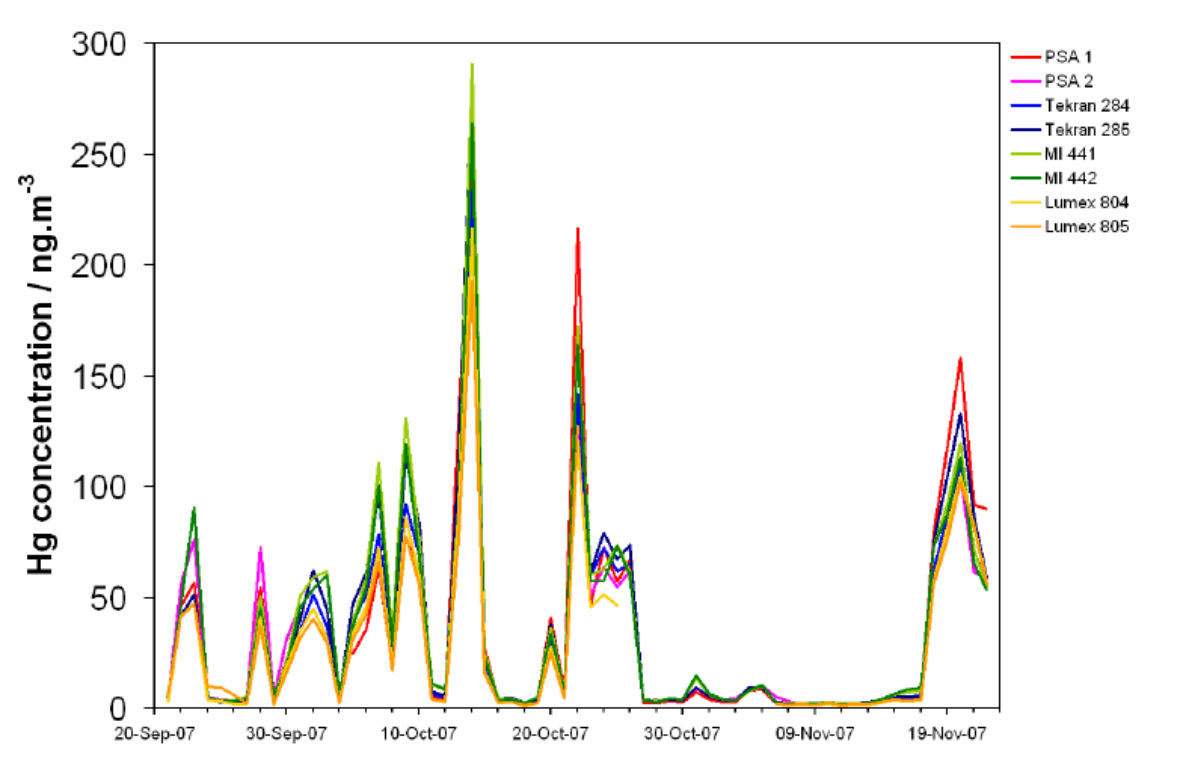

Figure 4. Daily mass concentration data from the Belgium TGM field trial.

For the evaluation of the Expanded Uncertainty WG 25 developed in the first step a methodology to estimate the overall expanded uncertainty of the method by calculating the random and non-random components of the uncertainty contributions from the field trial (for details on the method used see the Annex "Part F"). For the TGM measurements each instrument was assumed to be independent. These results are presented in **Table 4.**

Table 4: The average random and non-random deviations observed at each field trial location.

Sampling location	Average deviation	
	Random	Non-random
Italy	2.3 %	26.9 %
Spain	2.3 %	13.1 %
Sweden	1.6 %	7.5 %
Belgium	3.3 %	9.9 %

For completeness the average deviation between and within the different instrument types are also displayed in **Tables 5** and **6** below:

Tables 5: The average random and non-random deviations between the various instrument types tested at each field trial location.

Manufacturer	Average deviation between instrument types	
	Random	Non-random
PSA	2.2 %	10.0 %
Tekran	1.5 %	14.2 %
Mercury Inst.	2.3 %	18.7 %
Lumex	2.1 %	11.8 %

Table 6. The average random and non-random deviations within the various instrument types tested at each field trial location.

Manufacturer	Average deviation within instrument types	
	Random	Non-random
PSA	2.3 %	6.8 %
Tekran	1.2 %	8.7 %
Mercury Inst.	2.2 %	6.1 %
Lumex	1.1 %	4.4 %

Using the data from tables above, the four field trials yield expanded uncertainties at the 95 % confidence interval (assuming a coverage factor of k=2) of:

- **Italy: 54.3 % at an average TGM concentration of 1.9 ng.m-3**
- **Spain: 27.3 % at an average TGM concentration of 3.6 ng.m-3**
- **Sweden: 16.6 % at an average TGM concentration of 1.5 ng.m-3**
- **Belgium: 21.7 % at an average TGM concentration of 32 ng.m-3**

The uncertainty for each daily value at each location may be plotted and examined separately. This is done in the figure below (**Figure 5**).

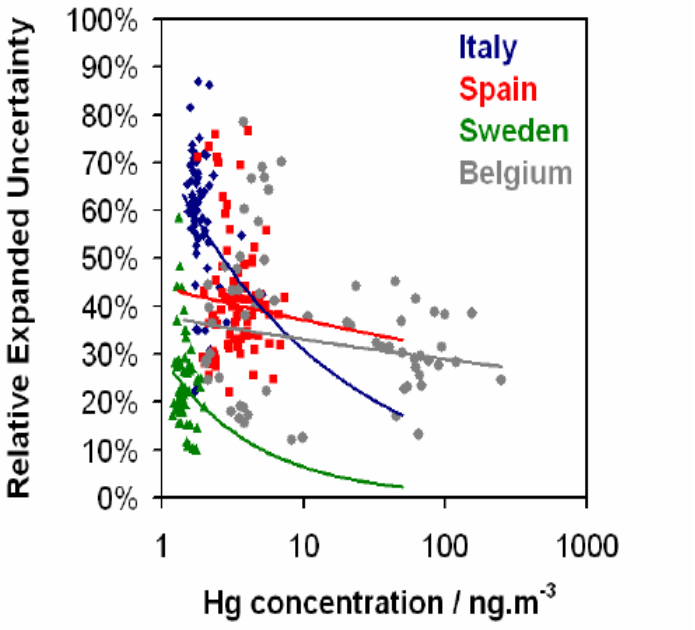

Figure 5. Expanded uncertainty against average measured daily concentration at the four field trial locations.

In order to meet the data quality objectives of the Fourth Daughter Directive the expanded uncertainty of the method must not exceed 50 %. Since no limit value is available at which to gauge this uncertainty requirement, we may instead determine the lowest concentration value

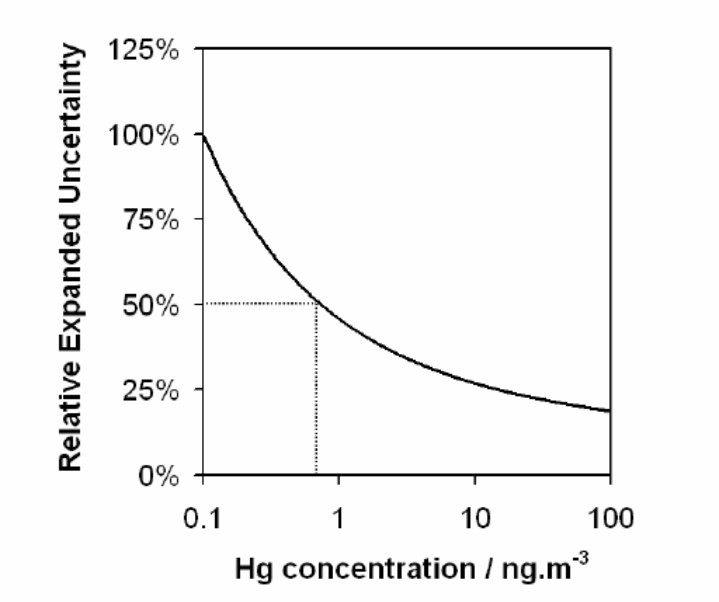

Figure 6: Expanded uncertainty against mercury concentration determined from the average of the trends exhibited by the four TGM field trials.

at which the uncertainty requirement can be met. The result of this analysis is shown in **Figure 6**.

This operation yields a relative expanded uncertainty of 50 % at a mercury mass concentration of approximately 0.75 ng.m-3. Therefore, this can be proposed as the lower range of the method.

The maximum observed daily average concentration on any individual instrument was approximately 300 ng.m-3 and so this could be used as the upper limit of the range of the standard method, although there is no reason why the method should not be applicable to higher concentrations provided the performance characteristics of the method are not compromised, gold traps are not saturated and the mass of mercury collected is not greater than the dynamic range of the instrument.

Over shorter collection periods, of approximately 5 minutes, concentrations as high at 4000 ng.m-3 were observed with no apparent impact on the instrumentation or measurement.
For more details regarding the determination of the statistical analysis of the standard method see the Annex “Part F”.

This Final Report of WG25 MVP consists of this Summary (*Part A_ Part A_WG25_Summary Field trial report_TGM.pdf*) and of the following five summary reports, which are available as individual PDF files (name given in brackets):

1.Summary report on the field tests in **Italy** (*Part B_WG25 Field trial report_TGM_Italy.pdf*);

2.Summary report on the field tests in **Madrid** (*Part C_WG25 Field trial report_TGM_Spain.pdf*);

3.Summary report on the field tests in **Sweden** (*Part D_WG25 Field trial report_TGM_Sweden.pdf*);

4.Summary report on the field tests in **Belgium** (*Part E_WG25 Field trial report_TGM_Belgium.pdf*). In Belgium voluntary measurements using manual method for TGM determination in ambient air were also performed. The results of these additional measurements are also included in the summary report.

5.Summary report on field trial statistical (*Part F_WG25 Field trial statistical report.pdf*).