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

CEN/TC 264/WG 25 „Standard method for the determination of mercury deposition 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.
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).

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 mercury deposition 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 6 months at two European measurement sites (one coastal/background and one local/industrial) over a period of 12 months. The working range of a standardised method should, in fact, cover 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 and analysis, were performed on the basis of Guidance documents (N 17 Guidance doc field tests Hg Deposition.doc), which were prepared by the Project Team (PT) of WG 25.
The purpose of described field tests was to develop a draft standard for mercury deposition, as defined in the Directive. The field validation included all steps of the draft standard including sample preparation, sampling and analysis of the samples. The field validation enables to demonstrate that the drafted reference method is fit for purpose. Hg deposition sampling took place 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 laboratories who participated in the WG 25 MVP are listed in **Table 1**, which also reports information concerning Hg deposition field trial location, sites criteria, coordinates and sampling periods.

Table 1. Laboratories participating in the WG25 – MVP

LABORATORY	MERCURY SITES	SITE CRITERIA	COORDINATES	CODE	PARTICIPATION IN (*)	SAMPLING PERIOD
Hg-Deposition						
SLOVENIA – IJS "Jozef Stefan" Institute, Department of Environmental Sciences, Ljubljana	Local/Industrial	Hot Spot	46.369°N, 15.083°E	Lab A	LT; PFT; FT; A	January 2007- September 2007
SWEDEN - IVL Swedish Environmental Research Institute, Göteborg	Remote/Background	EMEP Type	57.394°N, 11.914°E	Lab B	LT; PFT; FT; A	December 2006 - July 2007
UNITED KINGDOM - PS-ANALYTICAL				Lab C	LT; A (20% of samples from Lab A)	
GERMANY- UBA – UMWELT BUNDES AMT				Lab D	LT; A (20% of samples from Lab B)	

(*) 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 hg deposition 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. All sampling have been carried out with the same types of samplers and at each measurement site one lab was responsible for operating all samplers. Mercury was collected in special precipitation samplers.

Methods for different types of deposition samplers (bulk, Bergerhoff and wet only) were tested and the experiments for their evaluation were defined and optimised.

Bulk, Bergerhoff and wet-only samplers were used to obtain parallel precipitation samples for mercury analysis. It was proposed that equipment currently used in Europe have been tested over a 6 month period at both sites. Duplicate deposition samplers were used to collect for a

six months sampling period enough precipitation volumes for analysis by two laboratories to perform an extensive inter-comparison analysis exercise.
The aim of intercomparison was to evaluate the reproducibility of bulk, Bergerhoff and wet-only samplers as well as compare the sampling methods.

During the field tests, it was taken into account, as much as possible, standards or rules currently available in this area at a national or international level, and in particular the work being done within the CEN/TC 264/WG 20 and WG 21 on the deposition sampling methods for heavy metals and the polycyclic aromatic hydrocarbons, and within CEN/TC 264/WG 14 on the methods for determination of Pb/Cd/As/Ni in ambient air.
The number of deposition samplers used at each field trial location along with the total samples collected are reported in **Table 2**:

Table 2: Deposition Samplers used during the field trials by the two Laboratories.

LABORATORIES	DEPOSITION SAMPLERS		
	BULK	WET-ONLY	BERGERHOFF
SLOVENIA	2 (37 Samples)	2 (36 Samples)	4 (40 Samples)
SWEDEN	3 (59 Samples)	2 (38 Samples)	4 (32 Samples)

Weekly samples were taken, apart from the Bergerhoff samplers where approximately half the samples were taken monthly. Each site operator provided at least daily meteorological parameters (i.e. Precipitation amount in mm obtained by rain gauge). According to the document N 17, at each site:

- 20 % of Bulk samples has been sent to a second laboratory of the participating laboratories (see Table 1);
- 20 % of Wet only samples has been sent to a second laboratory of the participating laboratories (see Table 1);

- 20 % of the Bergerhoff samples has been sent to a second laboratory of the par ticipating laboratories (see Table 1).

Analysis of samples received from the two sampling sites have been performed following the analytical methods described in EMEP reference method (EMEP manual chapter 4.18.1) or ISO 17852 Water quality – Determination of mercury – Method using atomic fluorescence spectrometry (replaces EN 13506 Water analysis - Determination of mercury by atomic fluorescence spectrometry).

The analytical conditions were performed according to the documents CEN/TC 264/WG 25 N 900 and CEN/TC 264/WG 25 N 17 and related Annexes. Some changes from these documents and/or additional performances 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 weekly deposition rate measured at each site are detailed in the figures below (**Figures 1,2**).

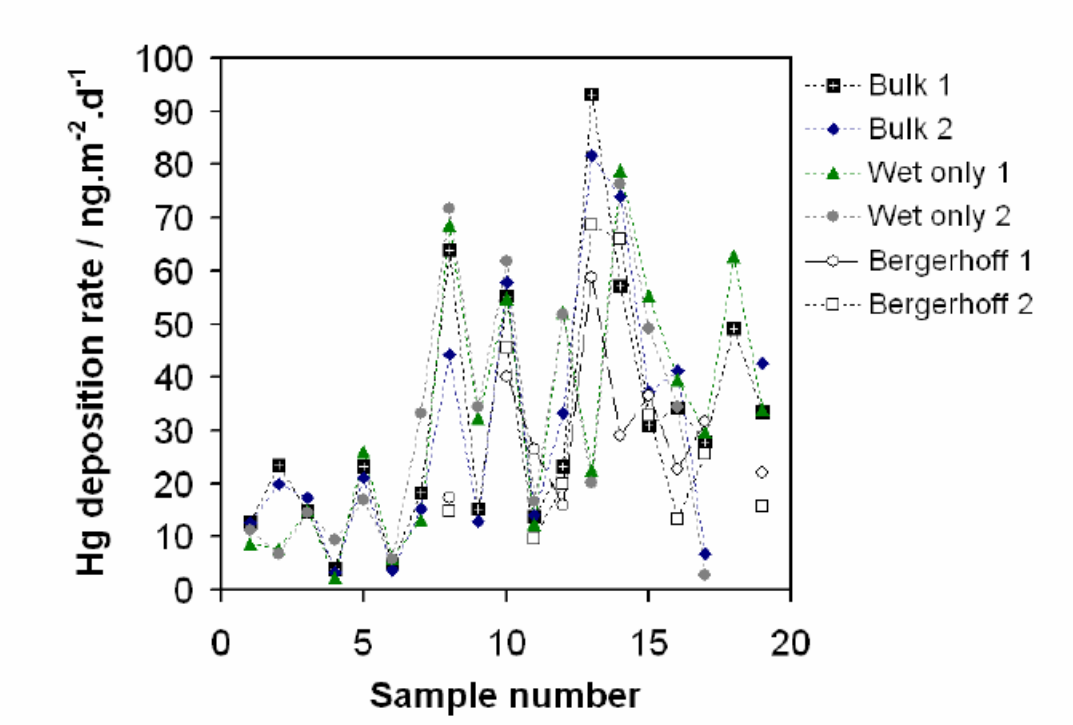

Figure 1. The weekly deposition rate results from the Slovenian deposition field trial.

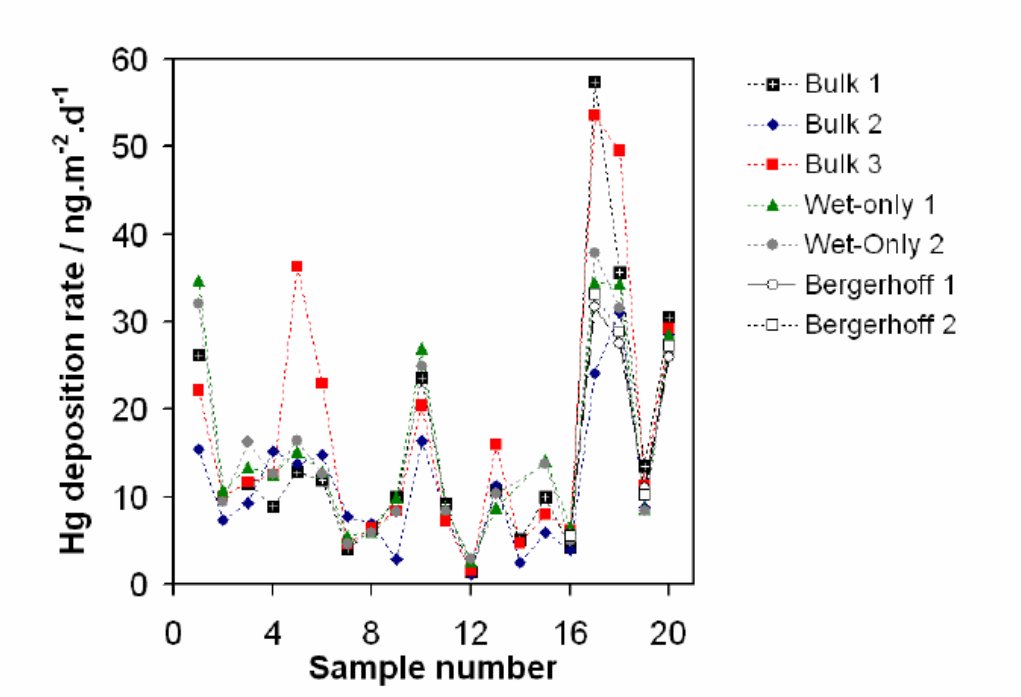

Figure 2. The weekly deposition rate results from the Slovenian deposition field trial.

For the statistical analysis of all mercury deposition data obtained at each CEN/TC 264/WG 25 European field trial site, the WG 25 develops a methodology to estimate the overall expanded uncertainty of the method for mercury deposition by calculating the random and non-random components of uncertainty from the field trial data. An additional component of uncertainty has been added to account for variability within the sampler types, and the uncertainty of the analysis process. **Tables 3, 4** show the average random and non-random bias within groups of samplers during the field tests in Slovenia and in Sweden, respectively. (For details on the method used see the Annex “Part D”).

Table 3. The average random and non-random bias within groups of samplers during the field trial in Slovenia.

Sampler type	Average deviation between sampler type	
	Random	Non-random
Wet-only	12.2 %	9.6 %
Bulk	7.7 %	9.4 %
Bergerhoff	9.0 %	19.0 %
Sampler type	Average deviation within sampler type	
	Random	Non-random
Wet-only	3.5 %	4.2 %
Bulk	3.6 %	0.4 %
Bergerhoff	7.2 %	1.7 %

Table 4. The average random and non-random bias within groups of samplers during the field trial in Sweden.

Sampler type	Average deviation between sampler type	
	Random	Non-random
Wet-only	1.2 %	4.0 %
Bulk	6.1 %	5.0 %
Bergerhoff	6.0 %	1.4 %
Sampler type	Average deviation within sampler type	
	Random	Non-random
Wet-only	1.8 %	1.7 %
Bulk	7.0 %	13.2 %
Bergerhoff	9.2 %	8.4 %

The exchange of samples between analytical laboratories result produced results that were in good agreement, considering the low concentrations being measured. Using the same process as described above, analysis of the results between laboratories yielded the following uncertainty characteristics:

• **Sweden:** samples exchanged between IVL and UBA showed a random uncertainty of 6.5 % and a non-random uncertainty of 4.4 %;

• **Slovenia:** samples exchanges between PSA and IJS showed a random uncertainty of 10.4 % and a non-random uncertainty of 0.7 %.

For the two field trials, the procedure (see Part D) yielded expanded uncertainties at the 95 % confidence interval of:

• **Slovenia: 39.8 % at and average deposition value of 30 ng.m^{-2}.d^{-1}**

• **Sweden: 44.2 % at and average deposition value of 17 ng.m^{-2}.d^{-1}**

In order to meet the data quality objectives of the Fourth Daughter Directive, a maximum expanded uncertainty of 70 % for the measurement method is permitted. This value occurs at approximately 10 ng.m^{-2}.d^{-1} for the extrapolation of the data performed. Therefore this value is proposed as the lower end of the applicable range of the standard method.
The maximum observed deposition rate on any individual sampler was approximately 1100 ng.m^{-2}.d^{-1} and so this could be used as the upper limit of the range of the standard method.

In conclusion, the absence of a limit value for Hg deposition at which to assess compliance with the uncertainty requirements of the Fourth Daughter Directive the calculated uncertainty against concentration relationships for the field trial results have been extrapolated to determine the lowest deposition rate at which the method meets the uncertainty requirements. This also then serves at the lower range of validity of the method. The upper limit of validity of the method has been nominally given by the highest deposition rate for deposition measurement. However is has been noted there is no reason why the method should not be applicable to higher concentrations provided the performance characteristics of the method are not compromised. Therefore the proposed ranges of the standard method is as follows in **Table 5**:

Table 5. The suggested measurement range for the mercury deposition standard, and the maximum measured value during the field trials.

Mercury deposition measurement range / $ng.m^{-2}.d^{-1}$		
Lower limit	**Upper limit**	***Max. Measured Value***
10	**1100**	***1100***

For more details regarding the determination of the statistical analysis of the standard method see the Annex “Part D”.

This Final Report of WG25 MVP consists on this Summary (*Part A_ WG 25_Summary Field trial report Hg-Deposition.pdf*) and on the following three summary reports, which are available as individual PDF files (name given in brackets):

1. Summary report on the field tests in **Slovenia** (*Part B_WG25 Field trial report_Hg-Deposition_Slovenia.pdf*);

2. Summary report on the field tests in **Sweden** (*Part C_WG25 Field trial report_Hg-Deposition_Sweden.pdf*);

3. Summary report on field trial statistical (*Part D_WG25 Field trial statistical report.pdf*);