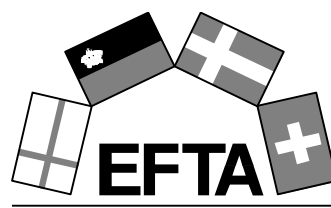


# CEN/TC 264/WG 14 „Standard method for the determination of Pb, Cd, As and Ni in ambient air“

## Final Report of the WG 14 Minimum Validation Programme Description and Results

Düsseldorf, August 2003

Contract B4-3040/2002/344744/MAR/C1  
covering the remaining 20 % of Step 3 of the closed  
Contract BC/CEN/11/258/1997/49.3



## Content

- Part A: Summary (PartA\_Summary.pdf)
- Part B: Summary report on the preliminary field tests (PartB\_PreliminaryFieldTests.pdf)
- Part C Summary report on the field tests in Madrid (PartC\_Madrid.pdf)
- Part D Summary report on the field tests in Avonmouth (PartD\_Avonmouth.pdf)
- Part E Summary report on the field tests in Berlin (PartE\_Berlin.pdf).  
In Berlin also voluntary measurements using three sequential low volume PM 10 samplers and two sequential high volume PM 10 samplers were performed. The results of this additional measurements are also included in the summary report.
- Part F Summary report on the field tests in Hoboken (PartF\_Hoboken.pdf).  
In Hoboken also voluntary measurements using three sequential low volume PM 10 samplers and two sequential high volume PM 10 samplers were performed. The results of this additional measurements are also included in the summary report.

# Part A:

## Summary

Within the framework of the EU/EFTA mandate M 258 CEN/TC 264/WG 14 was entrusted to establish a standard measurement method for the determination of Pb, Cd, As and Ni in ambient air according to the Community Directive 96/62/EC and the Council Directive 1999/30/EC relating to the limit values for lead (and sulphur dioxide, nitrogen dioxide and oxides of nitrogen and particulate matter) in ambient air.

For the validation of the recommended standard method WG 14 agreed on the Minimum Validation programme (MVP), which is financed by the European Commission (EC) under Contract BC/CEN/11/258/1997/49.3 – Step 3 and Contract BC/CEN/97/49.3. The WG 14 MVP consists on laboratory tests, preparation of field tests, preliminary field tests and field tests with sampling at four European measurement sites. The reports on the laboratory tests and the preparation of the field tests are included in the 1<sup>st</sup> Interim Report of WG 14, which was delivered to EC by end of 2000. The 2<sup>nd</sup> Interim Report of WG 14, which was delivered to EC by end of March 2002, includes the report on the preliminary field tests and partly on the field tests.

The individual steps of the MVP, like PM10 sampling, sample digestion (microwave digestion procedure) and analysis, were performed on the basis of Guidance documents, which were prepared by the Project Team (PT) of WG 14. The 1<sup>st</sup> Interim Report and the Final Report of the PT, which include the Guidance documents, were sent to EC by 2000-12-19 and by 2002-02-27 respectively. As analytical methods Graphit Furnace AAS and ICP-MS were taken into account. For the sampling process two types of filter material have been applied, Quartz Fibre and Membrane (Celluloseacetate) filters.

The sampling part of the preliminary fields in Madrid was performed by end of 2000. The sampling part of the field tests of the MVP took place at four European measurement sites, last in total over 80 days of sampling with 8 parallel samplers and was completed by end of 2001. The analyses of the exposed filter material (in total 640 sampled filters) were performed successfully by end of January 2002. Sampling took place in:

- Madrid (urban site), Spain, in May 2001

- Avonmouth (industrial site near Bristol), United Kingdom, in July/August 2001
- Berlin (urban site), Germany, in September/October 2001
- Hoboken (industrial site near Antwerp), Belgium, in November/December 2001

Four different sampling sites with distinct site characteristics were chosen in order to get as much information as possible on the performance of the reference method in different ambient conditions. The field trials have been carried out during the different seasons of a year to get information across different meteorological conditions.

The laboratories who participated in the WG 14 MVP are listed in Table 1.

**Table 1. Laboratories participating in the WG 14 MVP**

Laboratory	Code	Participation in *)
Centro Nacional de Sanidad Ambiental, Instituto de Salud Carlos III (ISCIII), Spain	Lab A	PpT, PIT, FT
UK Consortium (Casella Stanger / CRE Group Ltd. / Harwell Scientifics Ltd.), UK	Lab B	PpT, PIT, FT
Vlaamse Milieumaatschappij (VMM), Belgium	Lab C	PpT, PIT, FT
Umweltbundesamt (UBA-A), Austria / Umweltbundesamt (UBA-DE), Germany	Lab D	LT, PIT, FT
Health & Safety Laboratory, UK		LT

\*) LT Laboratory Tests  
 PpT Preparation of the Field Tests  
 PIT Preliminary field tests  
 FT Field Tests

The task of the MVP is to validate the standard method described in the EN of WG 14 and by this to show its suitability for the determination of Pb, As, Cd and Ni in ambient air at the limit values/monitoring thresholds fixed in the 1<sup>st</sup> and 4<sup>th</sup> 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.

For the evaluation of the Expanded Uncertainty WG 14 has developed a statistical model according to the GUM. In a first step all uncertainty contributions have been taken into account in order to evaluate the Combined Standard Uncertainties for all laboratories at the several sampling sites. In a second step the calculated and averaged Combined Uncertainties were used to extra- or interpolate the results to the limit value as required.

The Expanded Uncertainties of the standard method determined in the WG 14 MVP are listed in Table 2. The results show that the requirements regarding the (proposed) measurement uncertainties of the 1<sup>st</sup> Daughter Directive and the Position Paper on Cadmium, Arsenic and Nickel are fulfilled.

**Table 2. Expanded Uncertainties of the standard method determined in the WG 14 MVP at the limit value in %**

Element	AAS-Technique	ICP-MS-Technique	Requested
Lead	7	12	25
Cadmium	13	17	25
Arsenic	18	14	40
Nickel	21	9	40

The Repeatability and the Reproducibility of the standard method determined from the results of the WG 14 MVP are given in Table 3 and Table 4.

For more details regarding the determination of the Expanded Uncertainty, of the Repeatability and of the Reproducibility of the standard method see WG 14 Report "Statistical Evaluation of Field Test Data (Minimum Validation Programme)", which was delivered to EC by 2002-06-28.

This Final Report of WG 14 MVP consists on this Summary and on the following five summary reports, which are due to their big size available as individual PDF files (name given in brackets):

1. Summary report on the preliminary field tests (Part B, PartB\_PreliminaryFieldTests.pdf)
2. Summary report on the field tests in Madrid (Part C, PartC\_Madrid.pdf)
3. Summary report on the field tests in Avonmouth (Part D, PartD\_Avonmouth.pdf)
4. Summary report on the field tests in Berlin (Part E, PartE\_Berlin.pdf).  
In Berlin also voluntary measurements using three sequential low volume PM 10 samplers and two sequential high volume PM 10 samplers were performed. The results of this additional measurements are also included in the summary report.
5. Summary report on the field tests in Hoboken (Part F, PartF\_Hoboken.pdf).  
In Hoboken also voluntary measurements using three sequential low volume PM 10 samplers and two sequential high volume PM 10 samplers were performed.

The results of this additional measurements are also included in the summary report.

**Table 3. Repeatability and Reproducibility of the standard method determined in the WG 14 MVP**

		<b>AAS-Technique</b>		<b>ICP-MS Technique</b>	
Measure- ment site	Mean con- centration ng/m <sup>3</sup>	Mean Re- peatability *) %	Reproducibil ity %	Mean Re- peatability *) %	Reproducibil ity %
<b>Lead</b>					
Madrid	25	8	9	16	18
Avonmouth	85	5	8	9	10
Berlin	26	7	10	9	11
Hoboken	944	4	4	5	9
<b>Cadmium</b>					
Madrid	0,35	25	34	45	41
Avonmouth	3,78	8	10	21	24
Berlin	0,36	10	19	17	16
Hoboken	9,30	5	7	7	14
<b>Arsenic</b>					
Madrid	0,7	18	37	23	28
Avonmouth	1,7	15	22	10	12
Berlin	3,3	7	16	11	12
Hoboken	82,8	6	13	5	7
<b>Nickel</b>					
Madrid	1,5	93	94	88	89
Avonmouth	4,0	36	41	35	46
Berlin	3,6	22	40	25	37
Hoboken	15,8	15	21	8	9

\*) Repeatability averaged across all laboratories

**Table 4. Mean Repeatability and Reproducibility of the standard method determined in the WG 14 MVP across all measurement sites**

	<b>AAS-Technique</b>		<b>ICP-MS Technique</b>	
Element	Repeatability %	Reproducibility %	Repeatability %	Reproducibility %
Lead	6	8	10	12
Cadmium	12	17	22	24
Arsenic	11	22	13	15
Nickel	41	49	39	46