

WG 25 Determination of mercury in precipitation

Field tests at the Rao EMEP site in Sweden

Technical information

Field work

The Swedish measurement campaign where started at 4th of December 2006 and ended at the 4th of July 2007. Initially, three Bulk and two Wet only samplers were runned in parallel to collect weekly samples and four Bergerhoff dust collectors were used to collect 4 weeks samples. However, during last 5 weeks of the campaign two of the Bergerhoff samplers were used for collecting weekly samples. Altogether 129 precipitation samples where collected whereof 59 where Bulk samples, 38 Wet only samples and 32 Bergerhoff samples. Twenty-two samples were sent to UBA for analysis. Most of these samples were from one of the three bulk collectors. None of the samplers were splitted. Hence, all samples analysed by UBA were sent to Germany in their original collecting bottles.



Figure 1. Sampling of mercury in precipitation at the Rao EMEP site in Sweden. Rao is a coastal background measurements station located on the west coast (Lat: N 57° 23' 38", Long: E 11° 54' 51").

The measuring site is shown in Figure 1. The two Wet only samplers are shown to the left. The three black tubes are Bulk samples. The Bergerhoff samplers consist of fluorinated HDPE bottles of 2 l volume which are supported by steel baskets.

Cleaning of equipment, treatment of samples and analysis were performed following the WG 25, N17 REV3 and the EMEP manual. Routines regarding acid pre-additions to sample receivers are shown in Table 1.

Table 1. Acid addition prior to sampling

Sampler	Addition
Bulk	2.5 ml 30%-ig HCl, supra pur.
Wet only	7 ml 30%-ig HCl, supra pur + 93 ml MQ-water.
Bergerhoff 4/12-06 - 29/1-07	10 ml 30%-ig HCl, supra pur.
Bergerhoff 29/1-07 - 4/6-07	No addition

According to a German investigation acidic addition to the Bergerhoff sampler may give rise to passive uptake of elemental mercury. Their tests indicate that the best result is obtained without acid addition. After getting this information no acidic pre-addition was made to the Bergerhoff samplers.

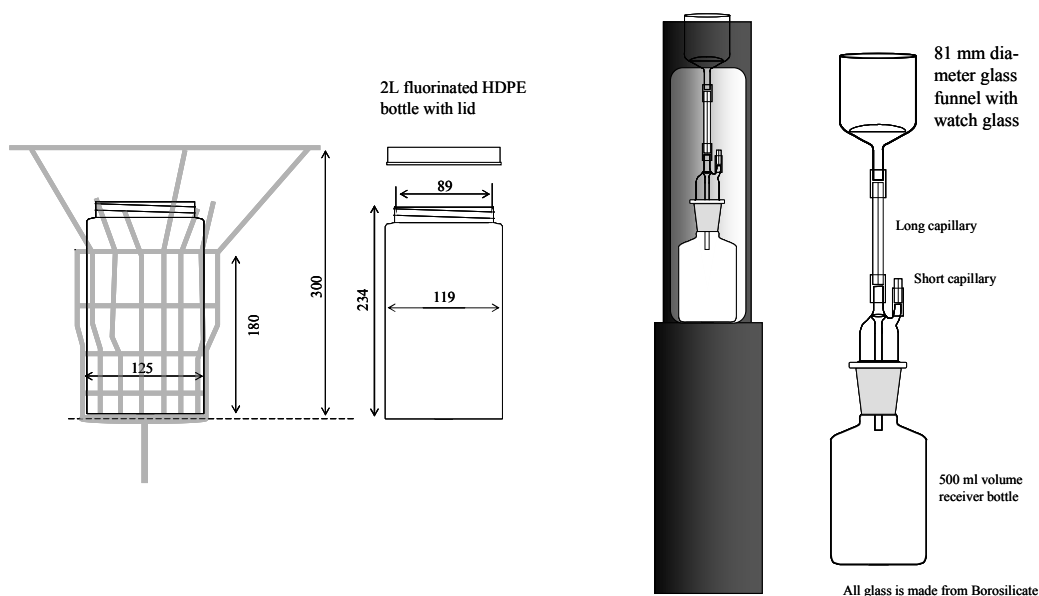


Figure 2. Left: Bergerhoff dust collector. The sampler consists of a collector bottle supported by a steel basket with a “bird ring”. Normally a Borosilicate glass vessel is used as the receiver. To avoid problems at low temperatures fluorinated HDPE bottles (of 2 l volume and 89 mm diameter opening) were used. The samplers were equipped with sun shields (not shown in the picture) to protect the sample from direct sunlight during sampling. Right: The Bulk collector parts are made from Borosilicate glass and housed in a PE cylinder. The sampler is electrically heated to protect samples from freezing during winter. The funnel and the receiver are connected through a capillary to prevent evaporation.



Figure 3. Eigenbrodt, NSA 181/KE Wet only collectors. The collectors are equipped with 240 mm diameter Borosilicate glass funnels and the precipitation samples are collected in 2 L volume FEP bottles. The sample receivers were kept at around 4 °C during sampling by help of the internal automatic heating and cooling system.

Mercury concentrations and precipitation amounts reported are corrected in respect to the pre-addition of acid.

Analysis; Calculation of $Hg_{(tot)}$

Before analysis the samples are oxidised by adding a bromine monochloride (BrCl) solution to the entire precipitation sample. Remaining BrCl is neutralised by adding a hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solution. Both these solutions contain small amounts of mercury. Hence, the mercury concentration in each batch of BrCl and $NH_2OH \cdot HCl$ solutions need to be determined to perform a correction. The BrCl addition also has a dilution effect that need to be considered.

Preparation of working standard from Nist standard solution is made in two dilution steps. The concentration of the working standard is calculated using equation 1.

- [Hg]_{s'} = Concentration of Nist standard Hg solution
- m_1 = Mass of Nist standard Hg solution (g)
- m_2 = Total mass of first dilution A (g)
- m_3 = Mass of dilution A used in the second dilution step (g)
- m_4 = Total mass of final dilution (g)
- [Hg]_s = Concentration of working standard ($ng\ g^{-1}$)

$$[Hg]_s = \frac{[Hg]_{s'} \times \frac{m_1}{m_2} \times m_3}{0.001 \times m_4} \quad ng\ g^{-1} \quad (1)$$

V_s = Volume of standard added for calibration (ml)
 R_s = Signal response from analysis of standard (integrated signal area)
 B_B = Bubble blank; signal from bubbler without addition of standard or sample (integrated signal area)
 RF = Signal response factor (ng^{-1})

$$RF = \frac{R_s - B_B}{[Hg]_s \times V_s} \quad \text{ng}^{-1} \quad (2)$$

$[BrCl]$ = The Hg concentration of the BrCl solution after neutralisation by an equal amount of $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (ng ml^{-1})
 V_{BrCl} = Volume of BrCl solution added to sample (ml)
 V_p = Volume of sample analysed (ml)
 V_{TOT} = Total volume of sample
 B_C = Chemical blank expressed as integrated signal area.

$$B_C = V_{BrCl} [BrCl] \frac{V_p}{V_{TOT}} RF \quad (\text{integrated signal area}) \quad (3)$$

B_{TOT} = $B_B + B_C$ (integrated signal area)
 R_x = Integrated signal area from analysis of sample
 V_p' = Volume of sample analysed corrected for dilution by BrCl and $\text{NH}_2\text{OH} \cdot \text{HCl}$ (ml)

$$V_p' = \frac{V_{TOT}}{(V_{TOT} + 2V_{BrCl})} V_p \quad (\text{ml}) \quad (4)$$

$$[Hg(\text{tot})] = \frac{R_x - B_{TOT}}{RF V_p'} \quad (\text{ng ml}^{-1}) \quad (5)$$

After calculating $Hg(\text{tot})$ the values were corrected for dilution in respect to pre-addition of acid. The precipitation amounts were also corrected in this regard. The uncertainty values reported were obtained using GUM calculations in which the uncertainties in all parameters above were considered. Results from quality control samples are shown in Annex 1.

Annex 1

Quality control sample exercises performed in conjunction to
WG 25 mercury precipitation sampling and analysis in Sweden,
2006-12-04 to 2007-06-04

Table 1. Replicate analysis of precipitation samples

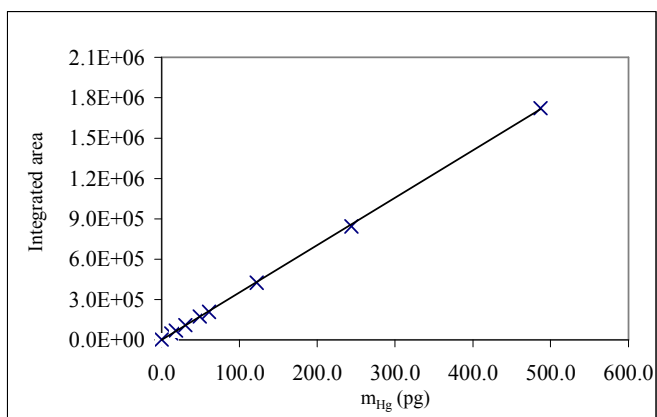
Day of analysis	Analysis 1	Analysis 2	*Precision of each analysis $\pm \text{ng l}^{-1}$	Rel. difference %
	ng l^{-1}	ng l^{-1}		
2007-01-12	21.8	21.2	0.9	2.8
2007-01-12	12.9	12.8	0.5	0.4
2007-03-03	7.7	7.5	0.5	3.2
2007-03-03	6.6	6.8	0.4	-2.5
2007-03-06	14.6	13.9	0.8	4.9
2007-03-06	17.7	17.3	0.9	2.8
2007-03-06	12.4	13.4	0.6	-7.5
2007-03-22	15.2	14.9	0.7	2.0
2007-03-22	6.3	6.4	0.4	-1.6
2007-04-19	15.0	15.3	0.5	-2.0
2007-04-20	10.8	10.9	0.4	-0.9
2007-04-25	3.7	3.7	0.3	2.5
2007-05-10	10.8	10.9	0.44	-0.9
2007-06-04	126	122	8.3	3.3
2007-06-28	7.77	7.66	0.38	1.4
Average relative difference (\pm %)				2.6

*According to GUM calculations

**Calibration of analysis set-up
including the CVAFS instrument**

2006-11-30

m_{Hg} pg	Integrated area
12.2	47493
18.3	69157
30.5	110014
48.8	173318
61.0	208657
122.0	425548
244.0	844338
487.0	1723378
0.0	2923

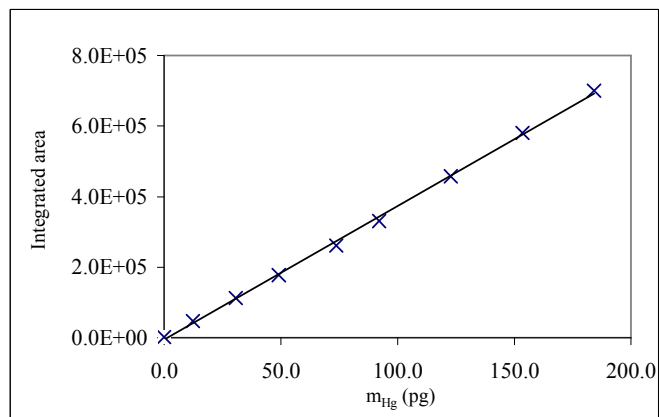


Slope (area pg^{-1})	t-value slope (area pg^{-1})	r^2	Intercept (area)	t-value slope (area)	n-2	Rel. precision of slope (at 95 % conf. level) \pm (%)
3521	17.0	0.99984	-16	3192	7	1.1

**Calibration of analysis set-up
including the CVAFS instrument**

2007-03-06

m_{Hg} pg	Integrated area
92.1	331158
122.8	457484
153.5	580824
12.3	47528
30.7	113043
49.1	177571
0.0	2590
184.2	700521
73.7	261454

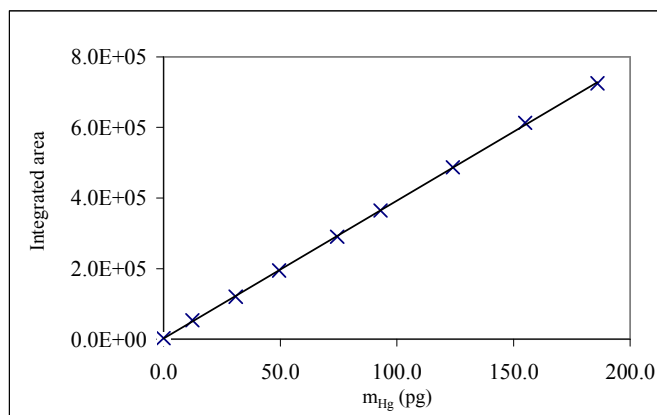


Slope (area pg^{-1})	t-value slope (area pg^{-1})	r^2	Intercept (area)	t-value slope (area)	n-2	Rel. precision of slope (at 95 % conf. level) \pm (%)
3787	47.5	0.9989	-5324	4749	7	3.0

Calibration of analysis set-up
including the CVAFS instrument

2007-03-22

m_{Hg} pg	Integrated area
12.4	53532
31.0	120532
49.6	194649
93.0	364521
124.0	487085
155.0	612563
0.0	2880
74.4	290412
186.0	725175

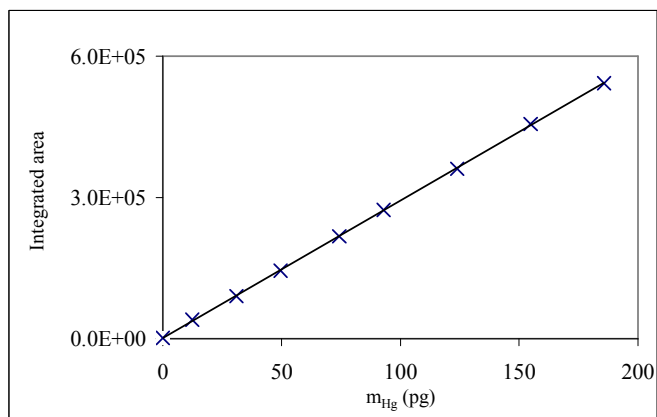


Slope (area pg^{-1})	t-value slope (area pg^{-1})	r^2	Intercept (area)	t-value slope (area)	n-2	Rel. precision of slope (at 95 % conf. level) \pm (%)
3904	16.2	0.99988	2127	1639	7	1.0

Calibration of analysis set-up
including the CVAFS instrument

2007-05-10

m_{Hg} pg	Integrated area
12.38884	40447
30.9721	90631
49.55536	144663
92.9163	273837
123.8884	361275
154.8605	456130
74.3	217593
185.8	542786
0	1941



Slope (area pg^{-1})	t-value slope (area pg^{-1})	r^2	Intercept (area)	t-value slope (area)	n-2	Rel. precision of slope (at 95 % conf. level) \pm (%)
2916	10.3	0.99991	1786	1038	7	0.8

Table 2. Quality Control samples

Analysis Date	Type of test	Hg(tot) ng l ⁻¹	*Precision ± ng l ⁻¹	Yield %
2006-12-08	Spike: Acid cleaned Bergerhoff bottle with 2 L MQ-water spiked with Hg standard. Stored for 10 days before analysis.	16.1	0.2	102
2006-12-08	Spike: Acid cleaned Bergerhoff bottle with 2 L MQ-water spiked with Hg standard. Stored for 10 days before analysis.	16.5	0.3	102
2006-12-08	Bottle blank: Acid cleaned Bergerhoff bottle with 2 L MQ-water. Stored for 10 days before analysis.	0.06		
2006-12-08	Bottle blank: Acid cleaned Bergerhoff bottle with 2 L MQ-water. Stored for 10 days before analysis.	0.06		
2006-12-12	Spike: Acid cleaned wet-only bottle with 2 L MQ-water spiked with Hg standard. Stored for 1 day before analysis.	20.3	0.7	103
2006-12-12	Spike: Acid cleaned wet-only bottle with 2 L MQ-water spiked with Hg standard. Stored for 1 day before analysis.	18.7	0.7	103
2006-12-20	Bottle blank: Acid cleaned wet-only bottle with 2 L MQ-water. Stored for 10 days before analysis.	0.13		
2006-12-20	Bottle blank: Acid cleaned bulk bottle with 0.5 L MQ-water. Stored for 7 days before analysis.	0.33		
2006-12-20	Bottle blank: Acid cleaned bulk bottle with 0.5 L MQ-water. Stored for 7 days before analysis.	0.33		
2007-01-12	Spike: Acid cleaned bulk bottle with 0.5 L MQ-water. Stored for 15 days before analysis.	21.8, 21.2	0.9	105
2007-01-12	Spike: Acid cleaned bulk bottle with 0.5 L MQ-water spiked with Hg standard. Stored for 15 days before analysis.	23.1	0.9	109
2007-01-12	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	12.9, 12.8	0.5	102
2007-01-12	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	1.98	0.1	107
2007-01-25	Field blank: wet-only	0.50		
2007-01-25	Field blank: Bergerhoff	0.90	0.1	
2007-03-06	Field blank: wet-only	4.3	0.2	
2007-03-06	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	12.40, 13.4	0.6	98.4
2007-03-22	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	13.30	0.6	106
2007-04-19	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	13.35	0.4	106
2007-04-19	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	1.98	0.1	107
2007-04-25	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	12.4	0.5	98
2007-04-25	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	2.06	0.1	111
2007-05-10	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	2.09	0.2	
2007-05-10	Field blank: Bulk	1.03	0.1	
2007-05-10	Field blank: wet-only	0.43	0.0	
2007-05-16	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	2.04	0.1	110
2007-06-20	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	1.98	0.1	107
2007-06-25	Analysis of standard reference material: BCR (1.85 ± 0.2 ng l ⁻¹)	1.99	0.1	108
2007-06-27	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	12.8	0.6	102
2007-06-27	Analysis of standard reference material: ORMS-3 (12.6 ± 1.1 ng l ⁻¹)	12.7	0.6	100

*According to GUM calculation