

## WG 25 Measurements of TGM at a Coastal Site in Northern Europe

(Field tests at the Rao EMEP site in Sweden)

### Technical information

#### *Field work*

The Swedish measurement campaign was started at the 11th June 2007 and ended at the 6th of August 2007. Two Lumex, two PSA, two Mercury Instruments and two Tekran instruments were tested in parallel while connected to a common air intake.



**Figure 1.** Measurements of TGM 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 instruments were placed inside a room in the measurement cabin. The room temperature was thermostatted to about 22 °C. All instruments were connected to the same inlet via a manifold made from Borosilicate glass which in turn was connected to an intake at the roof of the building via a 20 mm i.d. PTFE-tubing. The sampling air in-take was placed at about 4 m above the ground. A support flow of 13 litres per minute was all the time applied by help of an additional pump.

Prior to the measurements some initial tests were performed. The entire sample intake system was leak tested and found to be tight. The pressure drop through the intake and manifold was measured to be less than 1 kPa at the total flow rate, 29 L min<sup>-1</sup>, i.e. including the flow from all instruments and support flow. The sample flow rates of the instruments were measured using a pre-calibrated Drycal DC-Lite instrument and compared with the corresponding flow rate setting of each individual instrument. The result of this exercise is shown in Table 1, where standard flow rate refers to P = 101325 Pa and T = 293.15 K.

**Table 1.** Testing instrumental sample flow rates with a Drycal DC-Lite flow meter.

<b>Instrument</b>	<b>Instrumental set flow rate</b> L/min	<b>Type of flow regulation</b>	<b>Flow (P,T)</b> Drycal DC-Lite L/min	<b>Standard flow rate</b> L/min	<b>Rel. diff.</b> %
Tekran 284	1.000	MFR <sup>a</sup>	1.057	0.984	-1.6
Tekran 285	1.000	MFR <sup>a</sup>	1.071	0.997	-0.3
MI 441	0.666	Needle valve MFM <sup>b</sup>	0.710	0.660	-0.9
MI 442	0.666	Needle valve, MFM <sup>b</sup>	0.695	0.647	-2.9
PSA 1	0.800	MFR <sup>b</sup>	0.800	0.799	-0.2
PSA 2	0.800	MFR <sup>b</sup>	0.800	0.799	-0.1
Lumex 804 <sup>c</sup>	-	No regulation	5.248	-	-
Lumex 805 <sup>c</sup>	-	No regulation	5.672	-	-

<sup>a</sup>Mass flow regulation at P = 1 atm, T = 273 K. <sup>b</sup>Mass flow regulation and mass flow measurements at P = 1 atm, T = 293 K. <sup>c</sup>Lumex flow rates was obtained using external pumps.

All instruments except Lumex were calibrated using vapour mercury samples from a thermostatted mercury vapour source according to the N16 REV4 Guidance document, TGM field tests. The instruments were also maintained according to the N16 document (see Table A1 in Annex A), except for some changes, which where:

- Only one sample flow rate check were performed
- The sampling time with the PSA instruments were prolonged to 27 min
- The same sampling line was kept during the whole campaign

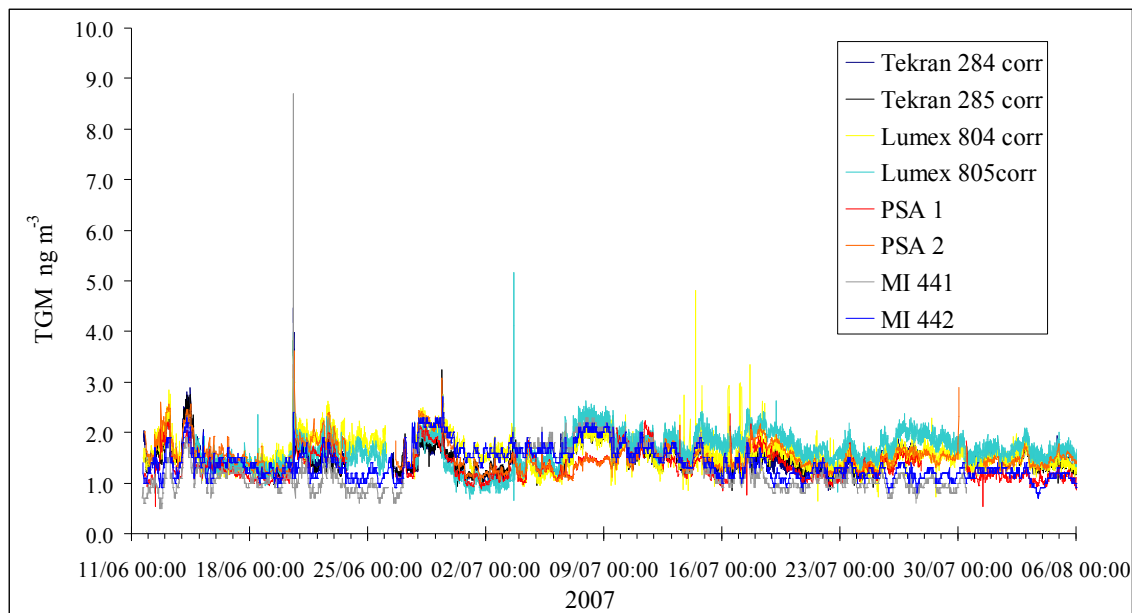
Some additional maintenance was made in collaboration with the instrumental providers, see Measurement Narrative in Annex B.

#### *Data report format*

All data were reported at standard conditions i.e. TGM values were calculated as ng per standard m<sup>3</sup> (P = 101325 Pa and T = 293.15 K). Hence, corrections in this respect were required concerning the Tekran and the Lumex instruments. No corrections in respect to the flow rate deviations shown in Table 1 were performed, however. The corrections regarding the Lumex instrument required measurements of the temperature (i.e. the temperature inside the instrument) and the ambient pressure. Small corrections (about 1%) to adjust the Lumex factory setting to the Dumarey equation as well as an equally small correction to compensate for internal pressure drop were also performed. The Lumex data (initially of 30 s time resolution) were recalculated and reported as 10 min average values.

## Results

Some weeks of preparation and initial tests, where followed by eight weeks of measurements yielding altogether 86400 individual data points. All data is shown in Figure 2.



**Figure 2.** TGM measurement result.

Evaluation of the measurement result from all campaigns is the task of NPL, UK. Only a preliminary investigation is presented here, see Table 2. The total mean value from all instruments is  $1.49 \text{ ng m}^{-3}$  and averages from individual instruments are confined within a range of  $\pm 15\%$  of this value. The relative standard deviation ( $1\sigma$ ) among all instruments is 8 %.

**Table 2.** Statistics

	Total averages of individual instruments  $\text{ng m}^{-3}$	Deviation of individual instruments in respect to the total average from all instruments %
Tekran 284	1.50	0.4
Tekran 285	1.45	-2.8
Lumex 804	1.59	7.1
Lumex 805	1.71	15.2
PSA 1	1.35	-9.3
PSA 2	1.54	3.3
Mi 441	1.36	-8.9
Mi 442	1.41	-5.1

## Annex A

**Table A1. Instrumental maintenance**

Maintenance procedure	Analyser			
	Tekran 2537 A	Mercury Instruments - UT-3000	LUMEX	PS Analytical - Sir Galahad II
Change dust filter	weekly	weekly	monthly	weekly
Change zero filter	monthly	yearly	yearly	-
Perform detector test	-	-	-	weekly
Check gas tight syringe	-	-	-	weekly
Check needle for blockages	-	-	-	weekly
Perform manual calibration	at beginning of campaign; every four weeks when you change gold trap	at beginning of campaign; every four weeks week calibration point check	manual self diagnostic at beginning of campaign	weekly
Automatic calibration check	every 25 hours	-	automatic baseline check (every 15 min)	-
Replace calibration port septum	every manual calibration	every manual calibration	-	every manual calibration
Replace calibration vessel septum	every manual calibration	before shipment	-	every manual calibration
Replace FEP sampling line	at beginning of campaign + at the end of the first month	at beginning of campaign + at the end of the first month	-	at beginning of campaign + at the end of the first month
Flow rate check	at beginning and end of campaign	at beginning and end of campaign	-	at beginning and end of campaign
Leak test	at each new site	at each new site	at each new site	at each new site
Carrier gas pressure	50 psi	-	-	40-60 psi
Perm source verification	every manual calibration	-	-	-
Replace gold trap	every four weeks	-	-	-
Download data	daily	weekly and clear memory	daily	daily
Frequency measurements	every 10 min	every 15 min	every 30 s	every 15 min
Trouble shooting	contact Tekran	check manual, contact MI	contact Lumex	contact PSA

## Annex B

### Measurement Narrative

Date, time	Action
18 May	1 PSA, 2 Lumex, 2 Mi and 2 Tekran instruments arrived from Spain to IVL. Later one PSA instrument arrived from Belgium which on request from PSA immediately was sent to England. The instrument was later sent back to Sweden and arrived sometime before 5 <sup>th</sup> of June.
22 May	The instruments were brought to the measurement site
31 May	Tekran 284 and 285, was equipped with new inlet filers and tested. Trap A of Tekran 284 yielded zero values. Later it was found to be due to a leak upstream the Au-trap A. Lumex 804, 805 were equipped with new inlet filters and tested. Due to software problems it was not possible to run more than one of the instruments on a Windows XP computer.
5 June	PSA 1 and 2 were equipped with new inlet filters, set up, calibrated and started by Evelyn Caldwell, PSA. It was found that the mercury concentration in the air inside the measurement station was about 20-50 times higher than the ambient. The reason for this is not known.
6 June	Tekran 284 and 285 were equipped with cleaned Au-traps, calibrated and started. Mi 441 and 442 were equipped with new inlet filers and started up.
8 June	The flow rate of all instruments were measured Lumex 804 was started connected to a Lap top (Win98) computer. Instead of the internal pump a Gast pump reduced to a flow a flow rate of 5.2 L min <sup>-1</sup> was used. Zero air was obtained by passing outside air through a Tekran zero air carbon trap.
11 June	<b>Start of the measurement campaign</b> The Mi, PSA and Tekran instruments were calibrated by injecting mercury from a common mercury vapour source.
13 June, 22:20	Lumex 804 stopped with error message
14 June, 16:30	Sergey Sholupov started Lumex 804 and 805 connected to a common computer (Win98) by help of a dual serial pc card (Silicom, S2S). The Lumex 805 was connected to the same zero air system as the Lumex 804. The Lumex 805 was equipped with an external pump with a flow rate of 5.7 L min <sup>-1</sup> . The pressure drop though the Lumex instruments was measured to be 12 mbar at 5.67 L/min.
15 June, 09:50	Tekran 284: No detector signal. The instrument was restarted 11:00 and seemed to be ok.
15 June, 18:10	Tekran 284 signal problem continues
18 June	Calibration of PSA 1 and 2. Calibration Mi441, 442. Tekran 284 was closed down, no signal. Restart Lumex 804, 805, 17:10:00
19 June, 15:30	Stop Lumex to update software. The time keeping was not satisfactory. Start with new software, 16:40:00
	New lamp was installed in Tekran 284. The instrument was started up and calibrated
	Restart Lumex 805, 17:00:00
20 June	Adjusting lamp on Tekran 284 and re-calibrating Septum replacements on PSA 1, Mi441 and 442
	Cleaning septum port on PSA 1 according to instructions from PSA. A new calibration program was installed and the instrument was calibrated.
21 June	Collected data
23 June, 18:20-18:30	Power failure, affecting the Tekrans and PSA 1 and 2.
26 June	Restart of Lumex 804, 805, 12:30:00, 12:40:00, respectively
13:30	Lamp adjustment on Tekran 285 and re-calibration
13:30	Calibration Tekran 285
13:45	Calibration PSA 1
13:50	Calibration Tekran 284
14:30	Start Tekran 284
15:00	Calibration and start PSA 2
15:10	Start Tekran 285
15:30	Calibration and start PSA 1
27 June, 14:30	Mi 441 stopped with error message: Sampling flow out of range. The pump voltage was measured and

	found to be too high (10.9 V), but seemed to be ok after restart. Au-traps in Mi 441 and 442 were replaced with new obtained from Mercury Instruments. The instruments were started up and running 3-4 measurement cycles before calibration.
18:20	Lumex 804, 805 connected to a new computer (Acer) to improve time keeping.
	Restart Lumex 804, 805, 18:30:00, 18:40:00, respectively
29 June	Mi 441 stopped with error message: Sampling flow out of range. The instrument was put off.
09:10	Leak test inlet line on PSA 1. Result: No leak
09:20	Exchange sample lines between PSA 1 and PSA 2. Result: No change
09:45	Calibrating MI 442. Restart 11:20
2 July, 10:00	The heating unit of the mercury source was broken. The temperature fell to -22 °C. It was not possible to restart after thawing.
17:50	A new heating unit was installed and everything seemed to work.
3 July, 13:50	A new pump was installed in Mi441. Result: OK, pump voltage within allowed range
14:00	In conjunction to a sudden power brake the cooling system of the mercury source brooked down.
17:20	A new cooling unit was installed. Result: working
17:30	All instrument were connected to power spike protection equipments
18:00	Tekran 284 was not possible to restart the screen was dead. The inner fuse on the internal fuse block found to be broken.
4 July 10:20	New fuse installed in Tekran 284. The instrument seemed to be ok.
10:50	Replacement of Au-traps in Tekran 284 (traps pair no. 3 replaced with traps pair no. 4).
11:15	Replacement of Au-traps in Tekran 284 (traps air no. 2 replaced with traps pair no. 1).
12:00	Calibrating Mi 441 <b>using the new source</b> (4.00 °C)
12:15	Calibration Tekran 284
12:30	Calibration Tekran 285 Start calibrating PSA 2 Start Mi 441
12:45	Recalibrating Tekran 284
13:10	Start Tekran 285
13:20	Start Tekran 284
6 July 10:00	Collecting data
	Restarting Lumex 804, 805, 11:00:00, 11:00:00, respectively
9 July 10:30	Current failure, all instrument went off except PSA 2 and Lumex 804 and 805.
10:40	Tries to restart failed. A main fuse supporting all instruments except PSA 2 seemed to be malfunctioning.
11:00	A new power port was tested and it seemed to work.
11:30	A new drawer (sent from PSA) with a tested Au-tube was installed in PSA 1
12:00	PSA 1 was restarted and a calibration was performed
11 July 09:05	New Ar bottle installed
	Restarting Lumex 804, 805, 11:30:00, 11:30:00, respectively
13 July 10:40	Calibrating PSA 1
16 July 10:30	Calibrating PSA 1, PSA 2, Tekran 284, 285
11:40	Restarting Lumex 804, 805, 11:40:00, 11:40:00, respectively
17 July 17:00	New Ar bottle
	Calibrating Mi 441, 442
20 July	Collecting data
23-07-07 12:00	Claibration PSA 1, PSA 2, collected data from all instruments
12:40	The Au-traps in Tekran 284 (traps no. 4) was replaced (with traps no 2). The instrument was started and allowed to run for one hour before calibration.
13:40	Both Lumex instruments were restarted (the time was about to run out)
14:20	Start calibrating Tekran 284
15:10	Start measuring Tekran 284
24-07-07 10:30	Calibration Tekran 284, 285
11:30	Start Tekran 284, 285
27-07-07 12:00	Replacing Au-traps in Tekran 285 (traps no. 1 was replaced with traps no. 3).
13:00	Calibrating Mi 441
13:10	Calibrating Mi 442
13:30	Start measuring Mi 441, 442
	No data from Tekran 285 during 13:00-13:30?

	13:50	Calibration Tekran 285
	14:30	Start measuring Tekran 285
30-07-07	10:00	Power failure 20:00 27-07-07. PSA1 and Tekran 284, 285 stopped. The Ar – gas bottle was emptied 01:35, 30-07-07.
	10:10	Tekran 285: the lamp circuit required adjustment
	10:30	Restarted Tekran 284. Start calibrating PSA 1, PSA 2
	11:40	Start calibrating Tekran 285
	11:40	Lumex 804, 805 were restarted, files: 804_30-07-07_11-40, 805_30-07-07_11-40
	12:00	Retrieved data from Mi 441, 442
	12:06	Restart Mi441, 442
	12:10	Started Tekran 285
31-07-07	11:45	PSA 2 Stopped measuring 2 cycles after calibration 30-07-07. PSA 1 yields low values, the signal is unstable and the pump flow is unstable (varies between 67-80%).
	13:54	Mi 441 suddenly stopped. Irrelevant flickering figures on the screen accompanied with a high signal. The instrument was turned off and restarted. On restart the screen was lit up but blank with warning signal. The instrument was turned off.
02-08-07	12:00	Possible to restart Mi 441, but all data was lost. Tried to recalibrate. Heating error: Check heating coil. The resistance over the heating coil was measured and found to be $\infty$ . The instrument was turned off.
	12:00	Signal and pump problems with PSA 1 remains.
04-08-07	08:45	Signal and pump problems with PSA 1
06-08-07	09:15	<b>End of campaign.</b> All instruments were turned off and the data were collected. In lack of an appropriate volume flow meter could the flow rate of the individual instruments not be determined. It is therefore important that this is performed in the beginning of the next measurement exercises in Belgium!
	17:15	All instruments were transported back to IVL
10-08-07	15:00	The Tekran and Lumex instruments and the MI Hg-source were shipped to VMM in Belgium. PSA instruments were shipped to PSA in England. Mi instruments were shipped to Mi in Germany.
13-08-07	13:30	Mi instruments delivered to Mercury Instruments in Karlsfeld, Germany.
14-08-07	14:35	Tekran and Lumex instruments delivered to VMM in Belgium.