

General Report for CEN/ TC 264 WG 25

Report of Lab B

“Reference Method for Determination of Total Gaseous Mercury in Ambient Air”

**Minimum Validation Programme CEN/ TC 264 WG 25 Field test at
Instituto de Salud Carlos III, University of Huelva (Campus de la Rábida),
Spain**

INSTITUTO DE SALUD CARLOS III

Description of the document

Title

Report of Lab B: Reference Method for the Determination of Total Gaseous Mercury in Ambient Air". Minimum Validation Programme CEN/ TC 264 WG 25.

Field test at Instituto de Salud Carlos III, University of Huelva (Campus de la Rábida), Spain.

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1. Background

This report is made by the Department of Atmospheric Pollution of Instituto de Salud Carlos III as response to a call by the CEN/ TC 264/ WG 25 for the preparation of the field test, which is part of the Minimum Validation Programme (MPV). The MPV is funded by the DG Environment of the European Commission.

2. Aim/ Overview

The field test is to develop a draft standard for TGM, as defined in the 2004/107/EC Directive.

Methods available for determining ambient concentrations of TGM were tested for 2 months at each site (in Spain 11 weeks) over a period of 12 months using automated equipment currently used in Europe for automatic determinations of mercury (TGM) levels in ambient air. Each laboratory used two units of each type of automated TGM instruments (for PSA only one instrument in Italy and Spain). The data obtained by each laboratory will be compared.

For the information on the performance characteristics field validation tests were carried out at four measurement sites in Europe (two coastal/background, in Italy and Sweden and two local/industrial sites, in Spain and Belgium). All sampling was carried out with the same type of sampler/ analyser and at each measurement site one lab was responsible for operating all instruments.

Site requirements were in accordance with the description in Directive 2004/107/EC. It was foreseen to perform the intercomparison at two background sites located, one in South Europe and one in North Europe and at two local/industrial sites, located in areas characterised by different types of emission sources.

3. Objective

- The general objective was to show the analytical results of the field test.

The report shows the results obtained by seven automatic analysers during a sampling period of 24 hours, from the 27th of February 2007 to the 15th of May 2007, performed in the University of Huelva (La Rábida campus).

4. Description of the site

The site was located in Huelva (figure 1), an agglomeration near a very high industrial area with old and quite new factories, including a chlor-alkali plant. The city was located in the south west of Spain near the Atlantic



shoreline (Cadiz Gulf) and undergo many Sahara dust episodes as well as typical inputs from sea breeze. The sampling site was in the University of Huelva (figure 2), sited at La Rábida, $37^{\circ} 16' N$; $6^{\circ} 57' W$, 2 km far from the chlor-alkaly plant.

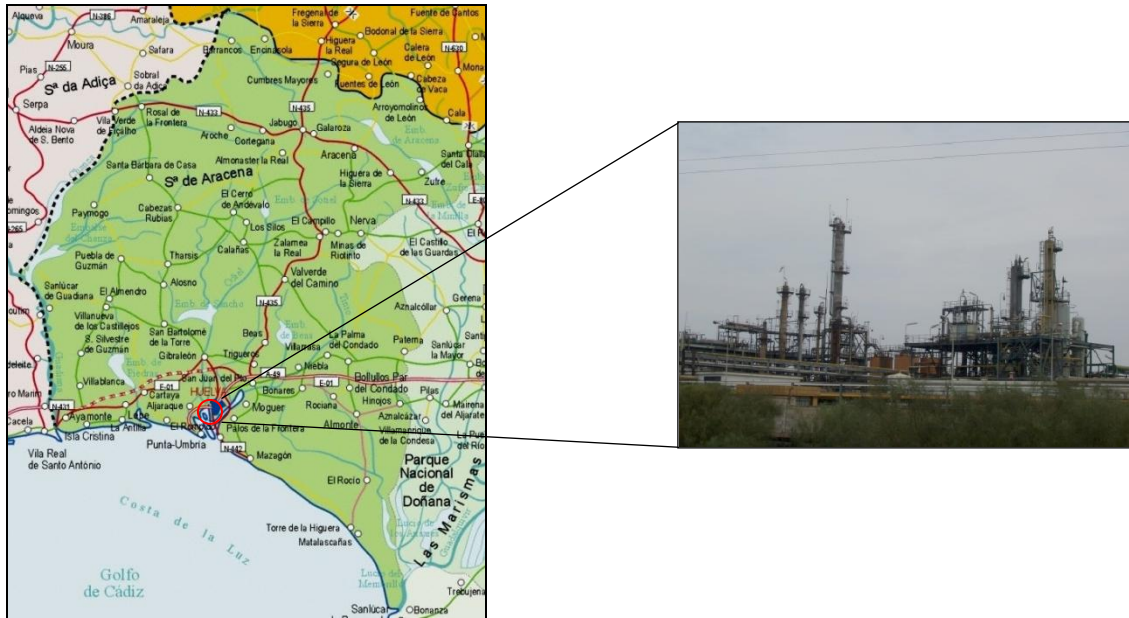


Figure 1. Sampling site at Huelva.



Figure 2. University of Huelva (La Rábida campus).

5. Instruments

The following instruments took part to the field trials:



- Two Tekran analyzers
- Two Mercury instruments analyzers
- Two Lumex analyzers
- One PSA analyzer

The instruments are showed in figures 3, 4, 5, 6 and the global overview in figure 7.



Figure 3. Parallel setup of two Tekran analyzers.



Figure 4. Parallel setup of two Mercury Instruments analyzers.



Figure 5. Parallel setup of two Lumex analyzers.



Figure 6. Setup of PSA Analytical analyzer.



Figure 7. Global overview.

6. Principles of Operation

The principles of operation of automatic analyzers are indicated in table 1

| | Cold Vapour Atomic Absorption Spectrometry (CVAAS) | Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) |
|---------------------|--|--|
| Tekran 2537 A | | X |
| Lumex RA-915+ | X | |
| Mercury Instruments | X | |
| PSA Analytical | | X |

Table 1. Principles of operation.

7. Analytical Conditions

The analytical conditions were performed according to the documents CEN/TC264/ WG25 N900 and CEN/TC264/ WG25 N16. Measurements were performed connecting the inlets of all seven analysers to a single manifold. In addition, meteorological parameters (temperature, wind speed and direction, relative humidity and solar radiation) were recorded.

8. Maintenance Procedure

The maintenance procedure fixed in the working group are indicated in the table 2.

| Maintenance procedure | Analysers | | | | |
|-----------------------------------|---|--|---|--|--|
| | Tekran 2537A | UT-3000 | Lumex | PSA, 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 fourth week when you change gold trap | at beginning of campaign; every third week calibration point check | manual self diagnostic at beginning of campaign | weekly | |
| Automatic calibration correction | weekly | - | automatic baseline check (every 15min) | - | |
| 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 (the same than Tekran) | |
| 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 of campaign | at beginning of campaign | - | at beginning 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 psi – 60 psi | |
| Perm source verification | every manual calibration | - | - | - | |



| | | | | |
|------------------------|-------------------|--------------------------|---------------|--------------|
| Clean cartridges | weekly | - | - | weekly |
| Replace cartridges | every fourth week | - | - | - |
| Download data | daily | weekly and clear memory | weekly | daily |
| Frequency measurements | every 5 min | every 15 min | every 30 s | every 15 min |
| Trouble shooting | contact Tekran | check manual, contact MI | contact Lumex | contact PSA |

Table 2. Maintenance procedure.

9. Results of field test

The results are in an excel file, called *Huelva data* (the data were sent to Richard Brown).

10. Graphs

10.1 First week

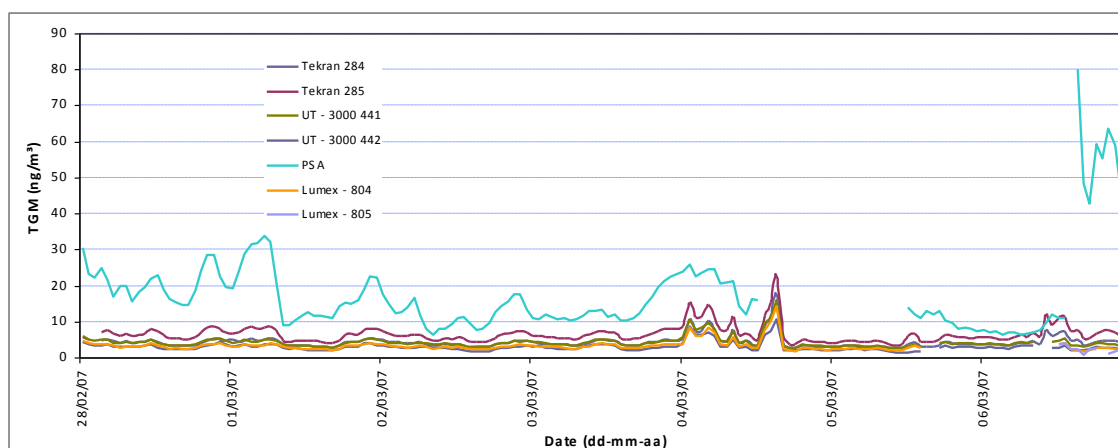


Figure 8. Results obtained by seven analyzers during the first week.

10.2 Second week

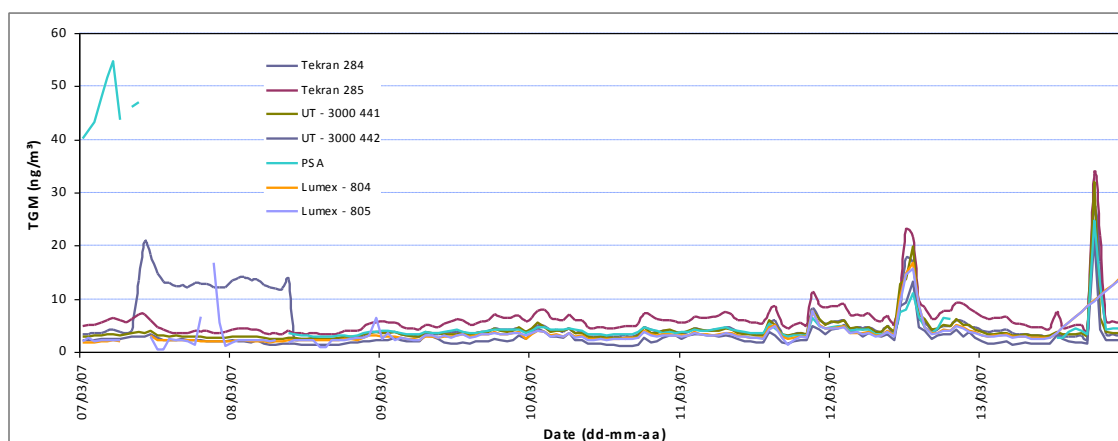


Figure 9. Results obtained by seven analyzers during the second week.



10.3 Third week

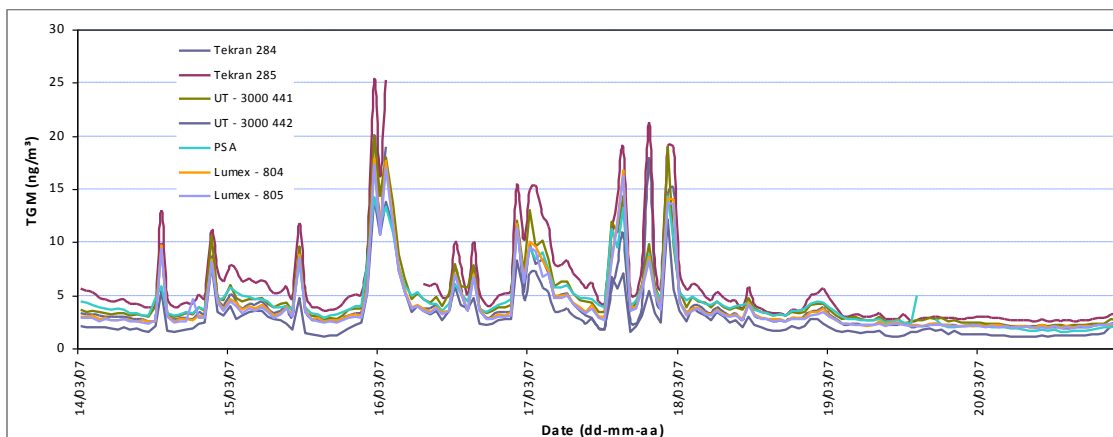


Figure 10. Results obtained by seven analyzers during the third week.

10.4 Fourth week

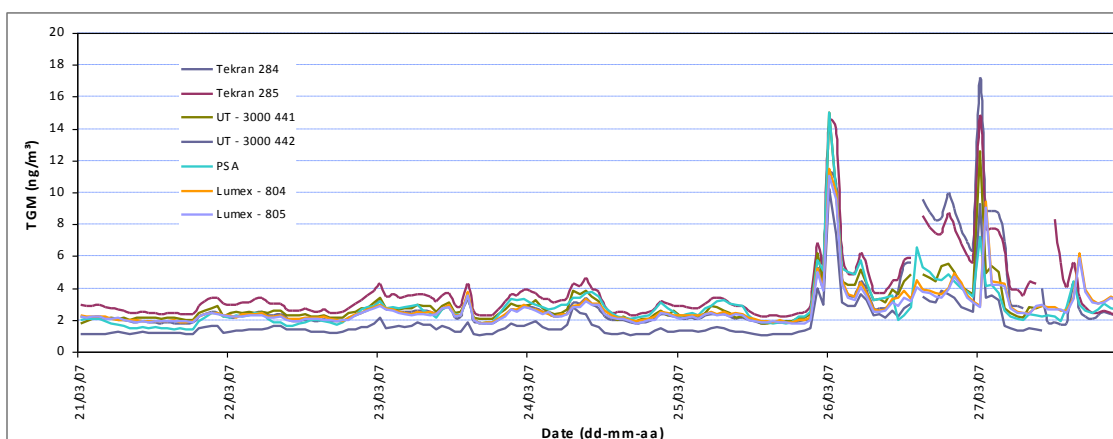


Figure 11. Results obtained by seven analyzers during the fourth week.

10.5 Fifth week

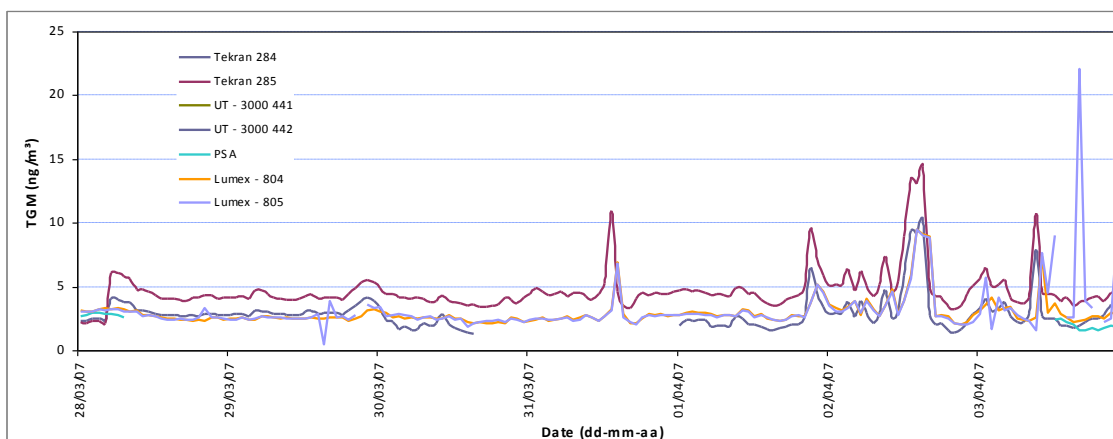


Figure 12. Results obtained by seven analyzers during the fifth week.



10.6 Sixth week

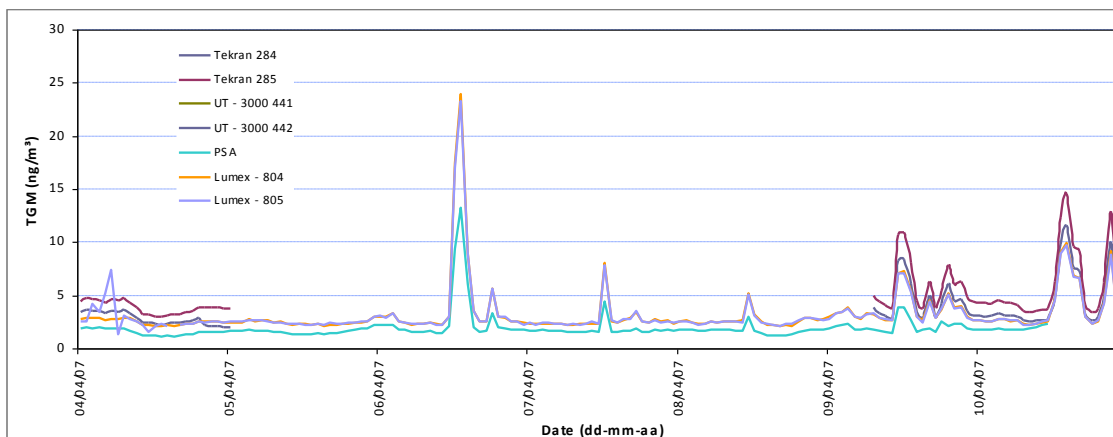


Figure 13. Results obtained by seven analyzers during the sixth week.

10.7 Seventh week

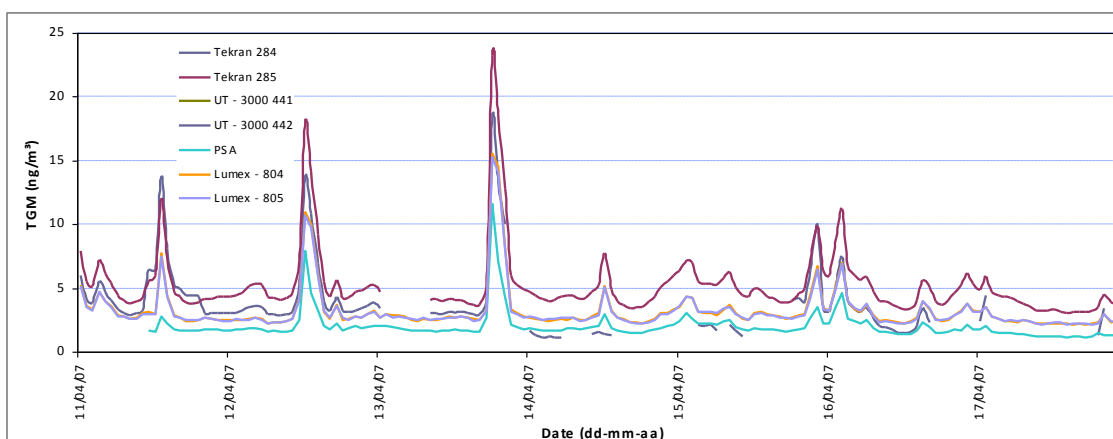


Figure 14. Results obtained by seven analyzers during the seventh week.

10.8 Eighth week

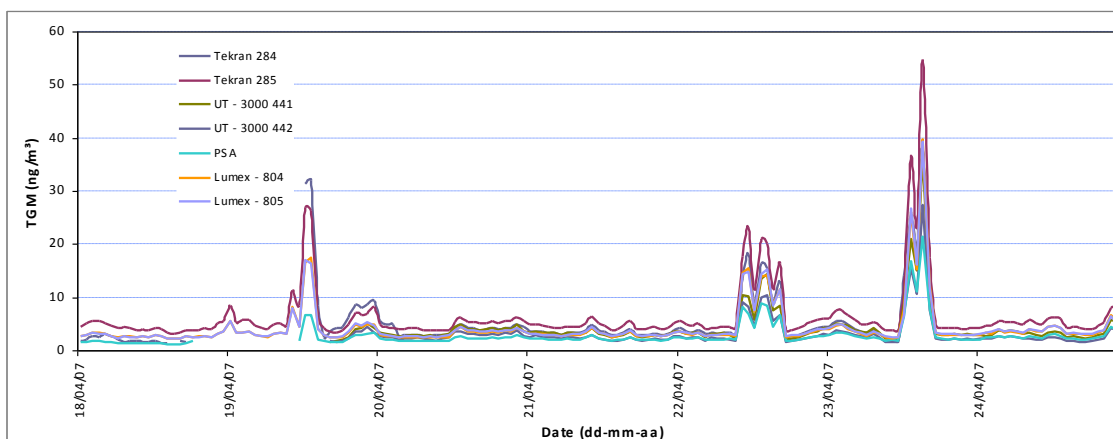


Figure 15. Results obtained by seven analyzers during the eighth week.

10.9 Ninth week

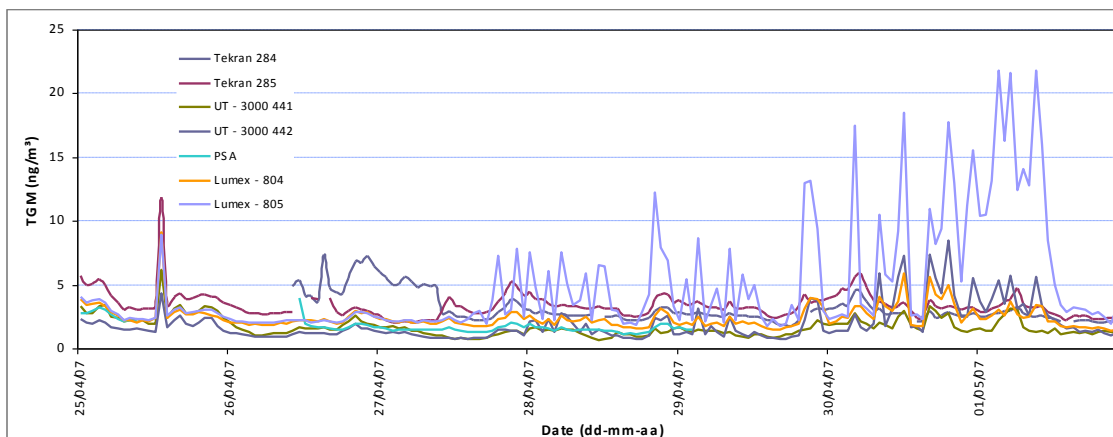


Figure 16. Results obtained by seven analyzers during the ninth week.

10.10 Tenth week

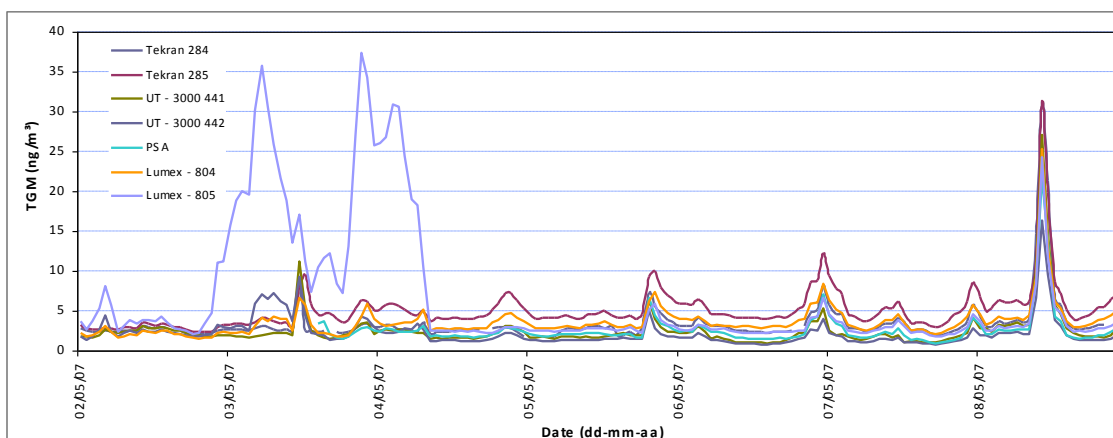


Figure 17. Results obtained by seven analyzers during the tenth week.

10.11 Eleventh week

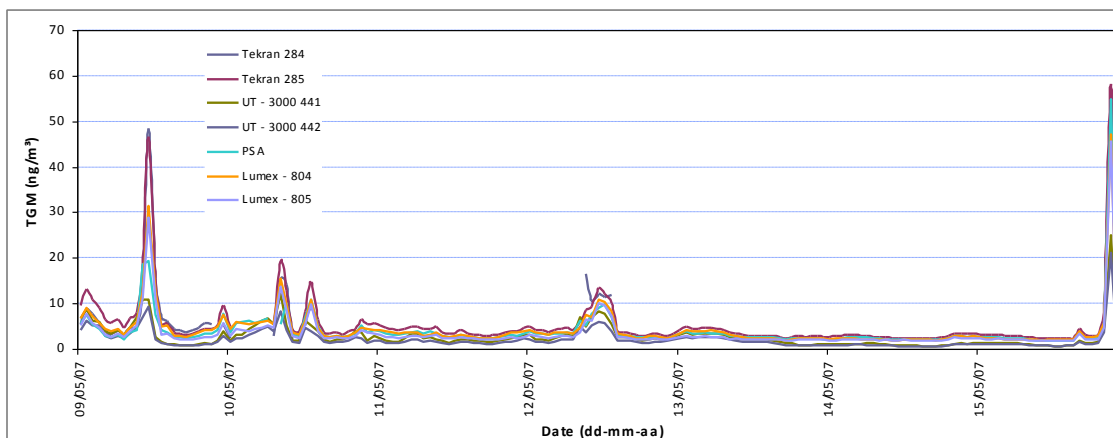


Figure 18. Results obtained by seven analyzers during the eleventh week.



11. Technical information

Lumex analyzer

At first of the campaign, we had problems with the Lumex software because when two equipments were connected to one PC, this one could not recognized to two equipments, due one equipment was recognized as “Microsoft intelligent mouse” which produced a “mad” movie of mouser pointer. This problem was detected in two different PCs. A Lumex technician installed a new software in the PC and the two equipment were working ok.

The Lumex 805 had not operated from 27th february to 6th march due “low radiation” was indicated. A Lumex technician repaired the instrument and it was working ok.

PSA

At first of the campaign, the mass flow controller was connected to COM 2 which has failed. So, we had to connect to COM 3 and it solved the problem. After three calibrations realized, the values obtained were higher than other equipments. Some test had been carried out following the indications of PSA campaign, but the instrument continued with the same problem, PSA were sent us the other drawer in order to changed it, at the end we didn't changed the drawer.

The 29th april the pump was broken and changed.

During the calibration of PSA we used our tekran calibration source because we hadn't any calibration source for the PSA analyzer.

During all the campaign we observed high consumption of argon (one cylinder of 10,5 m³ per week).

Mercury Instruments

At first of the campaign, we had some problems with hyperterminal, after we decided used only the datalogger of the instruments.

After one month (27th march), fuses burned in both instruments, we sent the instruments to Germany (3rd april) and restarted the measurements again (19th april), and finished the campaign without problems.



Tekran

In the early manual and automatic calibrations we observed high zero values.

In Tekran 284 the trap A measurement was 0 ng/m³ during the last three weeks, and the same for trap B during the last five days.

