



## **EnviSuM**

# WP3 Air quality and deposition/Activity 3.3 Urban measurements

# **Urban Air Quality Measurements**

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#### 1. Introduction

In this task we collected air quality measurement results in the pilot cities of the Tricity (Gdansk, Sopot and Gdynia) in Poland, Gothenburg in Sweden, and St. Petersburg in Russia to help to assess the effect of the new legislation and to evaluate the model results of Tasks 3.2 of this project. The air quality measurements were made during the years 2016–2018 near the city ports. Measured components for air quality included NO<sub>x</sub>, SO<sub>x</sub>, CO, O<sub>3</sub>, PM<sub>10</sub>, and PM<sub>2.5</sub>.

In order to reach comparability of the measurement results between all pilot cities, interlaboratory comparison of the measurement equipment were conducted by the Finnish Meteorological Institute (FMI). FMI maintains the accredited calibration and standard laboratory capable for providing SI-traceable calibration service for  $NO_x$ ,  $SO_x$  and CO measurements.

In addition, the scope of accreditation at the FMI calibration laboratory covers the weighing system of PM<sub>10</sub> and PM<sub>2.5</sub> filters obtained by reference samplers. The laboratory takes part in the interlaboratory comparison exercises at regular basis for the same gas compounds at the European Reference Laboratory for Air Pollution (ERLAP) in European Commission Joint Research Center (JRC), Ispra.

#### FMI delivered for the comparison

- facilities for conducting calibration for the measurements of NO<sub>x</sub>, SO<sub>x</sub>, CO and O<sub>3</sub>,
- reference samplers for side-by-side comparisons of PM<sub>10</sub> and PM<sub>2.5</sub> measurements with the station instruments to each of the pilot cities during the navigation season.

Calibration of the gaseous compounds and side-by-side comparison of particulate matter took place at one of the measurement station at each of the pilot cities. The comparison of the PM<sub>10</sub> and PM<sub>2.5</sub> measurements were conducted by parallel in-situ measurements of the reference method for PM as defined by the European Standard (EN) 12341 and the continuous PM analyzer by the pilot cities during a period of two months per site. The "Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods" by the EC working group of Demonstration on Equivalency was followed for the comparison. The protocol for the interlaboratory comparison was prepared by FMI and agreed with the partners before the start of the navigation season. The format of the presented data was decided

between the parties involved in advance. The final correction of the air quality results was based on the correction factors obtained from the interlaboratory comparison events at each of the pilot cities. The protocol for conducting the comparison studies is presented in Annex 1. The quality management system for the air quality measurements at each of the pilot cities was audited by the assessors from the FMI. The focus during the audit was to address on the activities for performing the QA/QC procedures at the selected pilot stations according to stated standards, i.e., European Standards (EN) prepared by European Committee for Standardization (CEN) or by National Standard. In the Tricity and in the city of Gothenburg, the European standards for the reference methods should be followed, whereas in St. Petersburg the national standards are used. The audit reports are presented in Annex 3.

#### 2. Measurement sites

The first comparison took place in Tricity (Gdansk), Poland, at the air quality station operated by Agency of Regional Monitoring of Gdansk Agglomeration (ARMAAG). The second comparison continued in Gothenburg, Sweden, at the measurement site operated by the City of Gothenburg. The third comparison took place in St. Petersburg at the air quality network operated by the State Company MINERAL. The comparison took place during a period of 2 months per each sites.

#### 2.1 Measurement site in Gdansk

The Agency of Regional Monitoring of Gdansk Agglomeration, ARMAAG (<a href="https://armaag.gda.pl/en/index.htm">https://armaag.gda.pl/en/index.htm</a>) is a foundation responsible for the air quality network in the Tricity area. The network includes 10 automated air quality stations, shown in Figure 2.1. The measurement station, AM8 was classified as an urban background station at Gdańsk - Wrzeszcz, ul. Leczkowa. Description of the station as well as the equipment can be seen in Annex 3. The comparison campaign took place from October 3 to November 27, 2016.



**Figure 2.1.** Air quality network at Tricity operated by ARMAAG and the site AM8 (red spot in the lower left figure) where the comparison study took place.

## 2.2 Measurement site in Gothenburg

The network (Figure 2.2a) is operated the City Gothenburg quality by (http://goteborg.se/wps/portal/start/miljo/miljolaget-i-goteborg/luft/). The network includes ten automated air quality stations. The comparison was conducted at two stations: at Gårda (Figure 2.2a) and at Femman (Figure 2.2b). The PM comparison was conducted at Gårda whereas the calibration of the gaseous analyzers took place at Femman. The Gårda site is classified as a traffic station and Femman as an urban background station. The comparison measurements took place at Gårda from December 14, 2016, to February 15, 2017.



**Figure 2.2a.** Air quality network at Gothenburg operated by City of Gothenburg and the Gårda site where the comparison study for particulate matter took place.



**Figure 2.2b.** Location of the station Femman where the calibration of the gaseous analyzers took place.

## 2.3 Measurement site in St. Petersburg

The air quality network in St. Petersburg (Figure 2.3) consists of 24 automated measurement stations run by the State Company Mineral (MINERAL). The comparison of particulate measurements against the reference method was conducted at two stations: PM<sub>10</sub> comparison was conducted at station No. 4 whereas PM<sub>2.5</sub> comparison took place at station No. 10. The comparison measurements took place from June 6 to August 3, 2018.



**Figure 2.3.** Air quality network at St. Petersburg operated by the MINERAL. The PM<sub>10</sub> comparison took place at station No. 4 and at station No. 10 PM<sub>2.5</sub> measurements were compared.

## 3. Comparison events and audits

## 3.1 Comparison of PM measurements against the reference method

The reference method to determine the mass concentration of particulate matter of the size category of  $PM_{10}$  and  $PM_{2.5}$  in the air is described in the EN 12341:2014 standard. The mass concentrations of suspended particulate matter in ambient air is determined by sampling the particulate matter on filters and weighing them by means of a balance. The sampling of the filters is conducted with the reference sampler including the size selective inlet, sampling flow system and control unit and filter holding system single filter or sequential filter holder. The weighing system and procedure for weighing the filters are described in the standard. The reference sampler used in this study in Gdansk and in Gothenburg for both  $PM_{10}$  and  $PM_{2.5}$  was a sequential type sampler SEQ47/50 by Sven Leckel, Ingenieurbüro GmbH, Germany; the layout of the reference sampler is shown in Figure 3.1a. In St. Petersburg, the reference sampler was PNS 3.1 made by Comde Derenda (Figure 3.1b).



Figure 3.1a. Sequential reference sampler Leckel SEQ 47/50.



**Figure 3.1b.** Sequential reference sampler PNS 3.1 by Comde Derenda.

The EN 12341 standard describes the environmental conditions for filter conditioning during the filter weighing process: temperature  $20 \pm 1$  °C, relative humidity 45 to 50 %. The weighing facility of the filters was made in house, consisting of the weighing chamber and the conditioning and control system. The weighing process of the filters is accredited according to EN ISO/IEC 17025 quality standard. The detailed description of the weighing system and procedure is given elsewhere (Waldén et al., 2017).

## 3.2 PM instruments for the comparison

#### **TEOM 1400ab**

The TEOM 1400ab, shown in Figure 3.2, uses the tapered element oscillating microbalance technique to measure the concentration of the particulate matter in the air. It is a direct mass measurement technique on a filter with real-time data output. The sample filter needs to be changed according to the loading percentile of the filter as indicated by the instrument or at regular intervals. By changing the sample inlet, the device is capable of making measurements of  $PM_{10}$  and  $PM_{2.5}$  at a sample flow of 1 m<sup>3</sup>/h. The sample inlet, type US-EPA, is recommended by the manufacturer and it was installed for the measurements. The measurement concentration range of the particles for the TEOM 1400ab can be up to 5 g/m<sup>3</sup>. To avoid condensation, the sample tube was heated (50 °C).



Figure 3.2. Thermo Scientific Ambient Particulate Monitor, TEOM 1400ab

The correction equation used in the software of the device by the manufacturer was of the form:  $y = a + b \cdot C$ , where  $a = 3 \mu g/m^3$ , b = 1.03 and C is the measurement signal. The factory settings were used at ARMAAG network (AM8 for PM<sub>2.5</sub> measurements). Instead of using the factory settings, the city of Gothenburg corrects the TEOM 1400ab signal according to equation  $y = 1.19 + 1.15 \cdot C$ . In addition to this, the amount of semi-volatile fraction in the air is estimated by using a factor of -1.87xTEOM(VCM), where TEOM(VCM) is the measurement results obtained by TEOM-FDMS instrument being able to estimate the semi-volatile fraction (VCM). The closest TEOM-FDMS instrument is at Femman which results is used to estimate the VCN fraction at Gårda station. These factors are defined by the Swedish National Reference Laboratory (NAQRL) at the Atmospheric Science Unit at the Department of Applied Environmental Science of Stockholm University to be used for correcting the results of TEOM 1400ab as equivalent with the Reference Method (ACES Report 4, 2012). The TEOM 1400ab was also demonstrated to be equivalent during the equivalence comparison studies in Finland (Walden et al., 2010; 2017).

#### FH 62 I-R

The ESM FH 62 I-R monitor by Thermo Fisher, USA, shown in Figure 3.3, uses the technique of  $\beta$ -attenuation (Kr-85 source). The FH 62-I-R is the new model from the original instrument Eberline FH62-I that was used at station AM8, for PM<sub>10</sub> measurements by ARMAAG. There has not been made any changes on the measurement technique that has influence on the performance of the instrument. The attenuation of  $\beta$ -rays by a filter is directly related to the amount of mass on the filter. The air sample is collected on the pure spot of the filter tape and is remains at the measurement/sample point until it is full loaded or after 24 hour sampling after which the filter tape rotates to bring a new pure spot on the measurement/sample point. The analysis of the sample, however, takes place cumulatively over the 24 h. To avoid condensation of water on the filter, the sampling tube is heated (35 °C). This process not only leads to the loss of water, but also to the loss of certain semi-volatile compounds such as ammonium nitrate. By changing the sample inlet, the device is capable of making measurements of PM<sub>10</sub> and PM<sub>2.5</sub> at a sample flow of 1 m<sup>3</sup>/h. The sample inlet was one of the commercial types designed

according to the EN-standards for PM<sub>2.5</sub> and PM<sub>10</sub>. The measurement range for normal operation is from  $0 \,\mu g/m^3$  to  $5000 \,\mu g/m^3$ .



Figure 3.3. FH 62-I-R

## IVL PM<sub>10</sub> sampler

The IVL PM<sub>10</sub> sampler, for weekly attendance, was constructed to meet the requirements from Swedish municipalities (Figure 3.4). Eight low cost sampling heads can be placed on the façade of a building, in street level, with the pump in a room inside the building. The IVL PM<sub>10</sub> sampler with the automatic changer can of course also be used for urban background measurements. The sampling head was tested during its construction at Ergonomics and Aerosol Technology's laboratory in Lund (Ferm et al., 2001). When the sampler met the cut-off curve for PM<sub>10</sub> in EN 12341, mass production started at a company with automatic lathes. IVL also successfully participated in the comparisons that were held. The sampler is now equipped with a mass flow regulator. Ambient temperature is continuously measured with a sensor connected to a controller that calculates the mass flow of air needed to meet the volume flow

of air through the sampling head that gives the correct cut-off curve. The average air pressure at the site is used in the calculation. Filters are chosen to enable subsequent analysis. In most cases Teflon filters are needed. Teflon filters have higher pressure drop than most filters. The IVL sampler therefore uses a low face velocity through the filter. The face velocity is only 17 cm/s. A low face velocity also minimizes sampling artefacts (volatilization from the filter).

The IVL PM<sub>10</sub> sampler with flow controller unit fulfills the criteria according to EN 16450:2017. The sampler was also demonstrated to be equivalence by the NAQRL study in Stockholm (ACES, 2012).



Sampling heads on a façade.

Mass flow controller (red) and controller box.

Figure 3.4. IVL PM<sub>10</sub> sampler

## **Grimm Environmental Dust Monitor, model 180**

The Grimm ambient dust monitor 180 is a stationary continuous fine dust measuring system for the simultaneous and continuous measurement of  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_1$ . The Grimm 180, shown in Figure 3.5, does not have  $PM_{2.5}$  or  $PM_{10}$  sampling heads according to EN standards. The sample inlet of the Grimm is the manufacturer's own design, but it has been tested against the  $PM_{10}$  reference method according to EN 12341 (LUBW, 2005). The sample flow rate of the Grimm was 1.2 l/min as stated by the manual and the sampling tube was inside the shield tube at ambient temperature. The concentration range for dust particles is from 0.1 to 1500  $\mu g/m^3$ . The instrument uses an optical technique, based on

light scattering, to divide particles into different sizes in diameter. The value of the refraction index of the particles, i.e., how much the velocity of light is reduced due to the reflection from the surface of the particles, has been programmed into the software. Specific algorithms are used to transfer the number of particles of certain size into mass. The calculated cut-off point curves are then applied to define the mass concentration for PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>. The sample air passes through an isothermal air drying system-during which moisture is extracted via a Nafion tube. This reduces the possibility of nucleonic condensation and therefore artificial growth/weight. The pump of the Nafion dryer starts at relative humidity of 50% reducing the relative humidity down to 35 %. The equivalency of the Grimm 180 is demonstrated by complete tests according to GRD report in Finland (Waldén et al., 2010; 2017).



Figure 3.5. Grimm Environmental Dust Monitor, model 180.

## 3.3 Calibration of the gaseous analyzers

The analyzers for measurements of gaseous air pollutants were calibrated according to the comparison protocol (Annex 1). Exception was made in St. Petersburg where this activity was not able to conduct because of the difficulties of transporting the calibration equipment and the gas standards through the Russian customs. Instead, a detailed study on the practice of the MINERAL for conducting the calibration in the calibration laboratory and the transfer of the calibration from the laboratory to the measurement station was conducted. The calibration facility used for calibration is shown the Figure 3.6.



**Figure 3.6.** Calibration facility of FMI used for calibration of the gaseous air quality analyzers at pilot cities. The lowest unit from the bottom is the ozone calibrator, the second lowest is the gas dilutor for preparation of calibration concentrations for  $SO_2$ , NO,  $NO_2$ , and CO gases. The third equipment is the  $NO_2$  analyzer and on the top is the data acquisition system.

## 3.4 Analysis of results

The analysis of the comparison results were conducted according to guidance document *Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, GDE*. To facilitate the use of the GDE for the demonstration of equivalence of the candidate methods (CM) against the reference method (RM) for PM monitoring, an Excel macro was available on the Commission web page (<a href="http://ec.europa.eu/environment/air/quality/legislation/assessment.htm">http://ec.europa.eu/environment/air/quality/legislation/assessment.htm</a>,). The macro (Beijk et al., 2006) allows the user to test of the equivalency for input pairs of data values of the CM and the RM. The GDE document was implemented into the Directive 2008/50/EC.

In case of gaseous pollutants, the calibration facility of the FMI including the gas standards was calibrated before and after visiting the pilot cities of Gdansk and Gothenburg. The pre-selected calibration concentrations cover the ranges described in the protocol and the same pre-selected concentrations were used both in the laboratory and the field calibrations.

## 3.5 Quality management system audit

The quality management system audits were performed in all three air quality networks in the pilot cities of the project both at the measurement stations to assess the quality of measurements and at the office to evaluate the level of documentation. The audits were performed in:

- Gdansk, station ARMAAQ/AM8, 2016
- Gothenburg, stations Gårda and Femman, 2017
- St. Petersburg, station No. 10, 2018

For Gdansk and Gothenburg, the requirements of EN standards as described in EU air quality legislation apply. For measurements in St. Petersburg, the national standards apply; however, in the audit the measurements were assessed against the EN standard to evaluate how harmonized the measurements are in the three cities.

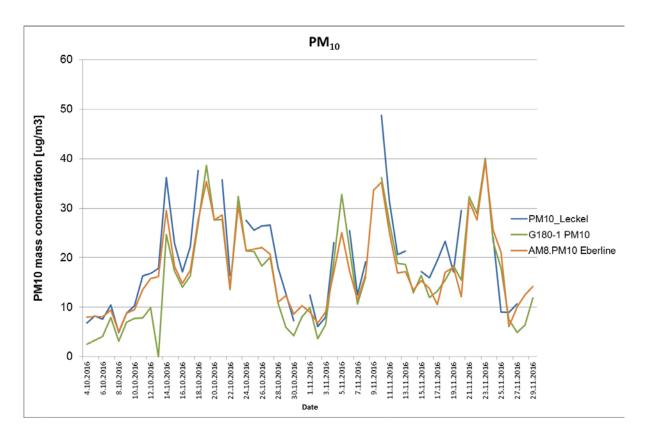
The audit topics were following; (1) general view on the measurements and station details, (2) personnel, (3) sampling, (4) instrumentation, (5) quality control, maintenance and calibrations of gas measurements, (6) zero gas, (7) PM measurements, (8) data collection, (9) documentation, (10) Quality Management System (QMS), and finally (11) a summary with comments and recommendations on the air quality measurements.

During the audit, the auditor interviewed the people in charge of the measurements and made observations on the measurements at the site and on the documents of the network. The audit subjects were documented in an audit questionnaire that was later verified by the network. The auditors were from FMI.

## 4. Results

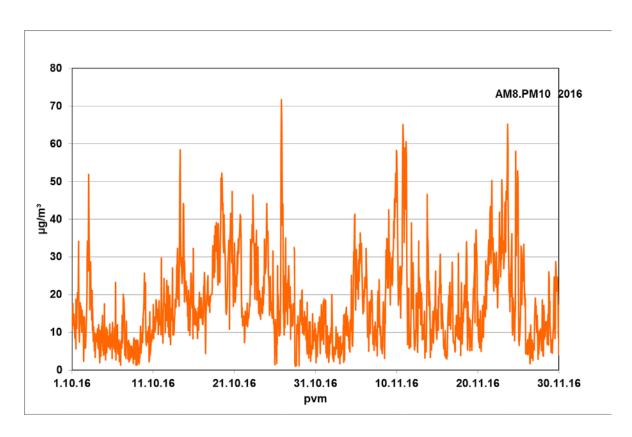
## 4.1 PM comparison in Gdansk

The protocol for the comparison campaign was followed. In Figure 4.1, the time series of daily averages for the site analyzer for  $PM_{10}$  measurements, the optical analyzer, and the reference method are presented from the city of Gdansk.

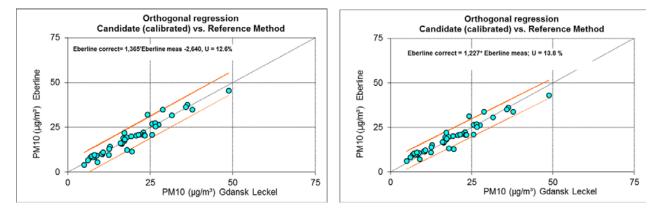


**Figure 4.1.** The daily average values of  $PM_{10}$  mass concentration for site analyzer Eberline, optical analyzer by Grimm, and the reference method at station AM8 in Gdansk.

The hourly average values of  $PM_{10}$  for site analyzer Eberline FH 62-I is presented in Figure 4.2. The orthogonal regression analysis between the site analyzer and the reference method analyzed according to the GDE are shown in Figure 4.3.

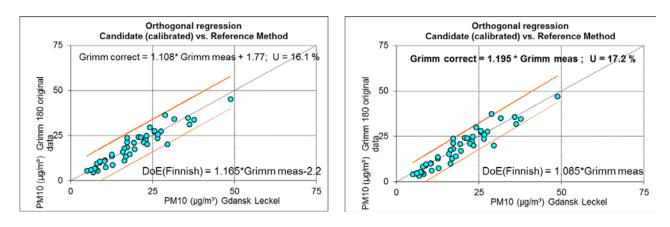


**Figure 4.2.** Hourly averages for  $PM_{10}$  mass concentration measured by site analyzer Eberline FH 62-I at AM8, Gdansk.



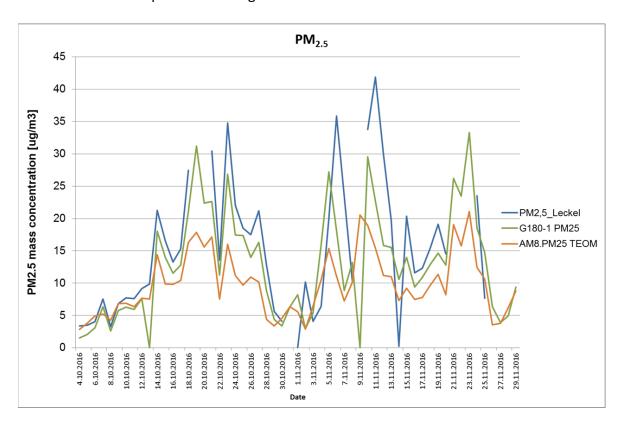
**Figure 4.3.** Orthogonal regression analysis between the site analyzer for PM<sub>10</sub> at AM8 and the reference method. In the left, the calibration equation of type y = ax + b, where y is the corrected value of Eberline FH 62-I, a is the slope of the calibration equation, x is the raw value of Eberline FH 62-I and b is the intercept. In the right the calibration equation is forced through the origin where the calibration equation is type y = ax.

Figure 4.4 presents the similar results for the Grimm 180 as was used for supporting analyzer.



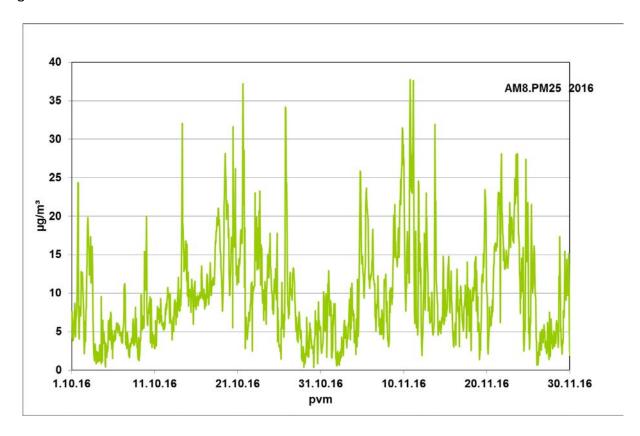
**Figure 4.4.** Orthogonal regression analysis between the Grimm 180 and the reference method, see text in Figure 4.3.

The time series of daily averages for the site analyzer for  $PM_{2.5}$  measurements, the optical analyzer, and the reference method are presented in Figure 4.5.

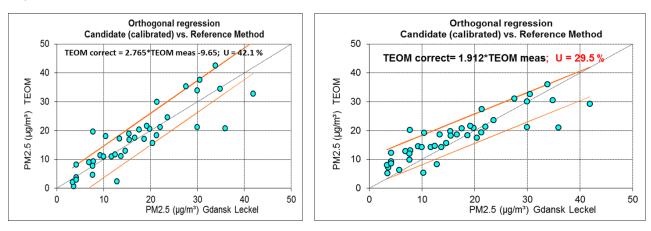


**Figure 4.5.** The daily average values of PM<sub>2.5</sub> mass concentration for site analyzer TEOM 1400ab, optical analyzer by Grimm and the reference method at station AM8 in Gdansk.

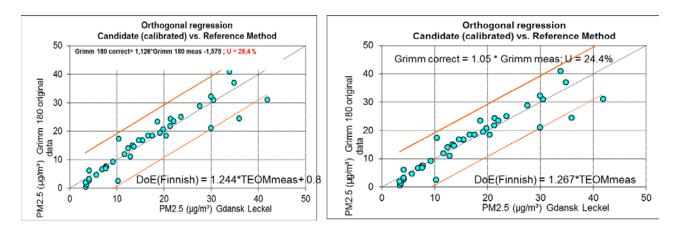
The hourly average values of PM<sub>2.5</sub> for site analyzer TEOM 1400ab is presented in Figure 4.6. The orthogonal regression analysis between the site analyzer and the reference method analyzed according to the GDE are shown in Figure 4.7 as well as between the optical analyzer and the reference method in Figure 4.8.



**Figure 4.6.** Hourly averages for  $PM_{2.5}$  mass concentration measured by site analyzer TEOM 1400ab at AM8, Gdansk.

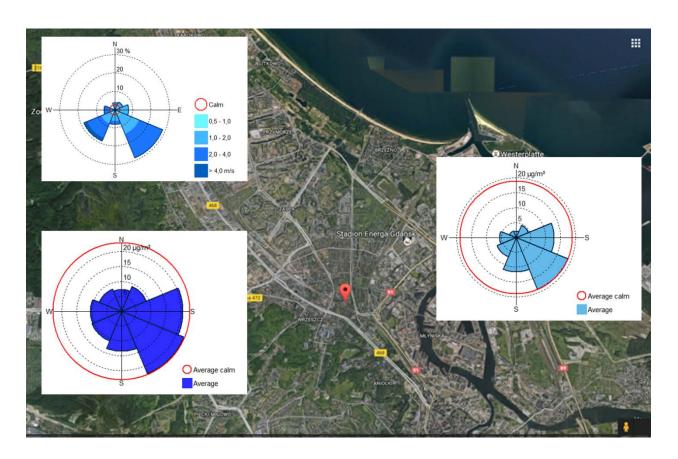


**Figure 4.7.** Orthogonal regression analysis between the site analyzer for PM<sub>2.5</sub> at AM8 and the reference method, see text in Figure 4.3.



**Figure 4.8.** Orthogonal regression analysis between the Grimm 180 and the reference method, see text in Figure 4.3.

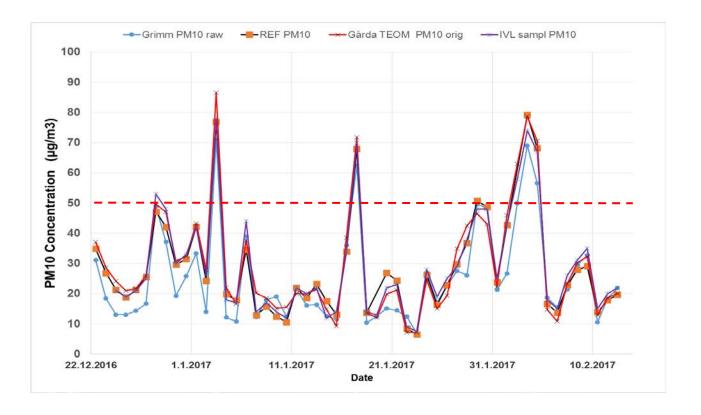
The wind rose and the pollution roses of  $PM_{10}$  and  $PM_{2.5}$  calculated as 10-min averages from Grimm 180 are shown in Figure 4.9.



**Figure 4.9.** Pollution roses for the wind speed, mass concentration of  $PM_{10}$  and  $PM_{2.5}$  at station AM8.

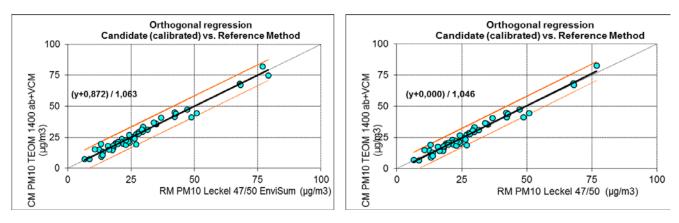
## 4.2 PM comparison in Gothenburg

The Protocol for the comparison campaign was followed. In Figure 4.10, the time series of the daily averages for the site analyzer for  $PM_{10}$  measurements (TEOM 1400ab), the reference method, and the optical analyzer (Grimm 180) are presented from the city of Gothenburg.

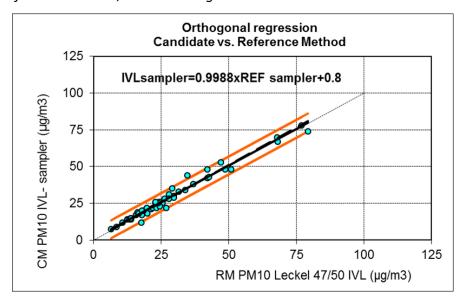


**Figure 4.10.** The daily average values of PM $_{10}$  mass concentration for site analyzer TEOM 1400ab, optical analyzer Grimm 180, IVL PM $_{10}$  sampler, and the reference method at station Gårda in Gothenburg.

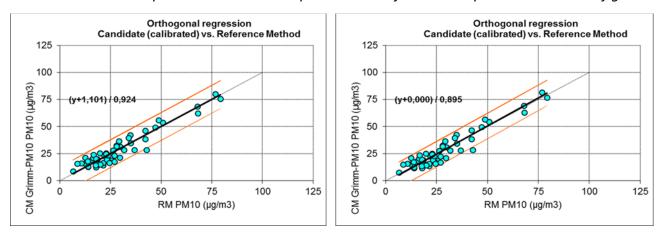
The orthogonal regression analysis between the site analyzer TEOM 1400ab, the IVL sampler, and the Grimm 180 against the reference method analyzed according to the GDE is shown in Figures 4.11–4.13, respectively.



**Figure 4.11.** Orthogonal regression analysis between the site analyzer TEOM 1400ab for PM<sub>10</sub> at Gårda station and the reference method, see text in Figure 4.3.



**Figure 4.12.** Orthogonal regression analysis between the IVL sampler for  $PM_{10}$  and the reference method. The relationship between the IVL sampler and the reference sampler is shown in the figure.



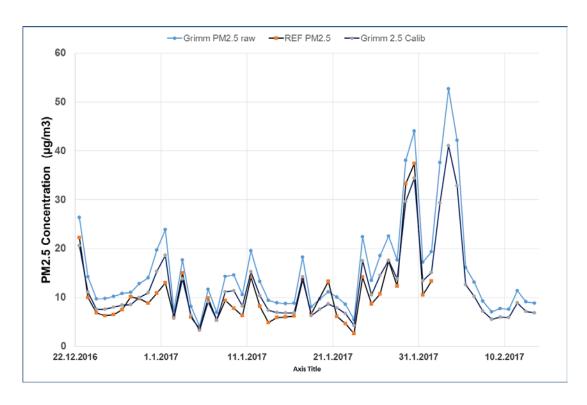
**Figure 4.13.** Orthogonal regression analysis between the Grimm 180 and the reference method, see text in Figure 4.3.

The summary of the orthogonal regression analysis for  $PM_{10}$  comparisons at Gårda station is presented in Table 4.1.

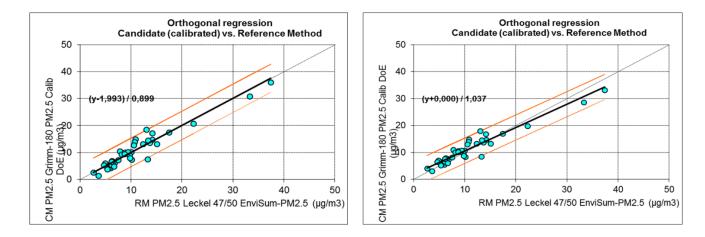
**Table 4.1.** Summary of the analyzed data with the orthogonal regression analysis for TEOM 1400ab, IVL sampler, and Grimm 180. Measured data indicates the regression analysis between the PM instruments and the reference sampler according to the relation y = ax + b, where y is the result of the PM instrument, a is the slope, x is the result of the reference sampler and b is the intercept. Calibrated data give the correction function (full equation and slope through origin) for the PM instrument. The red font is an indication for the non-satisfactory result. To meet the data quality objectives according to EU air quality directive is indicated by "Pass" and failure to meet the requirement is indicated by "Fail).

Comparison test: PM <sub>10</sub>	Criteria	Gårda: TEOM 1400ab+VCM	IVL sampler	Grimm 180	
Concentration range	μg/m³	0 - 90	0 - 90	0 - 90	
Measured data					
Slope	significant (Yes/No)	1,0628	0,9988	0,9524	
Intercept	significant (Yes/No)	-0,87	0,8	-1,5869	
Expanded relative uncertainty	≤ 25%	15,6 %	10,7 %	24,57 %	
Fail/Pass	≤ 25%	Pass	Pass	Pass	
Calibrated data					
Calibration: equation		0,941y + 0,82		1,05y + 1,666	
Expanded relative uncertainty	≤ 25%	13,6%		22,3 %	
Fail/Pass	≤ 25%	Pass		Pass	
Calibration: slope through origin		0,961y		1,102y	
Expanded relative uncertainty	≤ 25%	9,3%		21 %	
Fail/Pass	≤ 25%	Pass		Pass	
Precalibration equation		Y=(X-1,19)/1,15)-1,87*PMref : PMref from TEOM 1405D at Femman			

In Figure 4.14, the time series of daily averages for the  $PM_{2.5}$  measurements with the reference method and with the optical analyzer is presented from the city of Gothenburg. The orthogonal regression analysis between the optical analyzer and the reference method analyzed according to the GDE are shown in Figure 4.15.

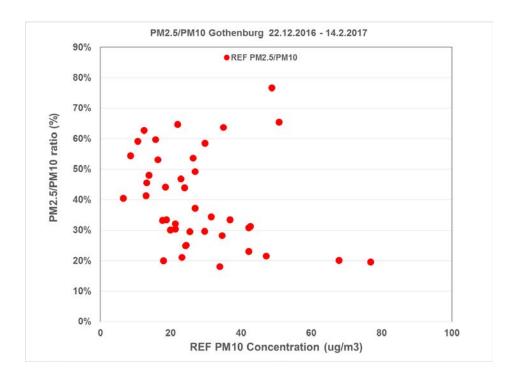


**Figure 4.14.** The daily average values of  $PM_{2.5}$  mass concentration for optical analyzer Grimm 180, and the reference method at station Gårda in Gothenburg. Grimm  $PM_{2.5}$  raw means that the results is not corrected by any calibration factor, while results are corrected with the calibration function at Grimm 2.5 Calib (Walden et al. 2017).



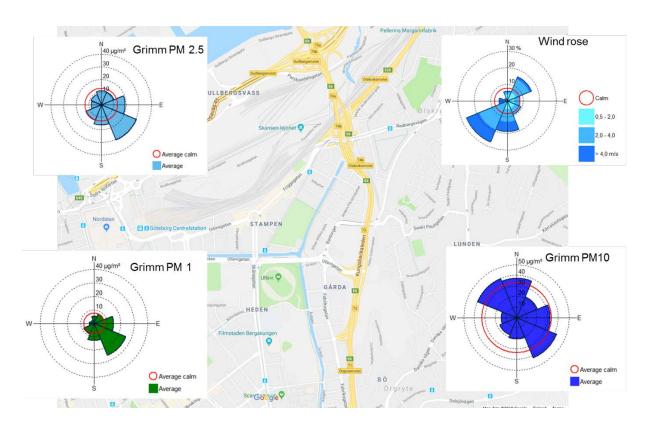
**Figure 4.15.** Orthogonal regression analysis between the Grimm 180 (corrected by calibration) and the reference method for  $PM_{2.5}$ , see text in Figure 4.3.

The ratio of  $PM_{2.5}/PM_{10}$  is calculated from the results of the reference method, presented in Figure 4.16.



**Figure 4.16.** The ratio of  $PM_{2.5}/PM_{10}$  calculated from the Reference method.

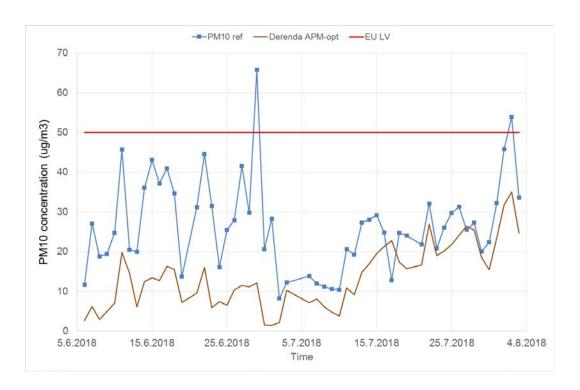
The wind rose and the pollution roses of  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_1$  calculated as 10-min averages from Grimm 180 are shown in Figure 4.17.



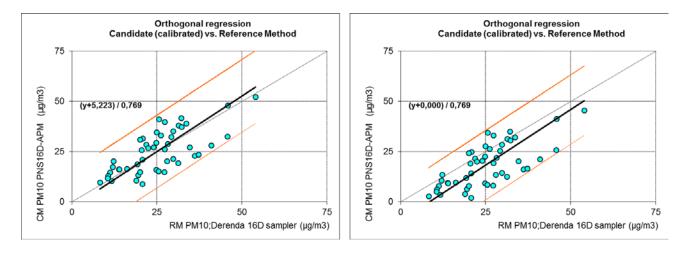
**Figure 4.17.** Wind and pollution roses for the wind speed, mass concentration of  $PM_{10}$  and  $PM_{2.5}$  at station Gårda.

## 4.3 PM comparison in St. Petersburg

The Protocol for the comparison campaign was followed. In Figure 4.18, the time series of daily averages for the site analyzer for  $PM_{10}$  measurements APM2 optical method and the APM2 filter method as the reference method is presented from the city of St. Petersburg. The orthogonal regression analysis between the site analyzer APM optical method against the APM filter sampling as reference method according to the GDE is shown in Figure 4.19.



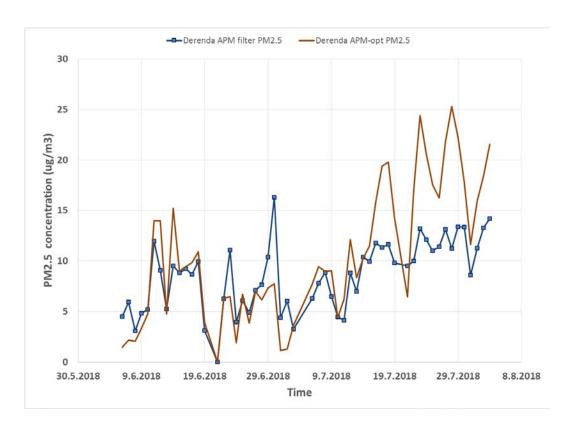
**Figure 4.18.** The daily average values of  $PM_{10}$  mass concentration for site analyzer APM2 optical method and the APM2 filter method as the reference method at station No. 4 in St. Petersburg. Red line represents the EU limit value of  $PM_{10}$  daily average concentration.



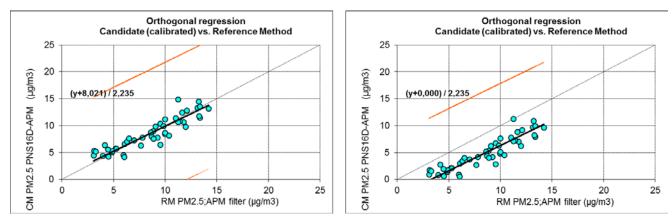
**Figure 4.19.** Orthogonal regression analysis between the APM optical method and the APM filter sampling as reference method for PM<sub>10</sub>, see text in Figure 4.3 except that in the figure right the slope is not forced through the origin.

In Figure 4.20, the time series of daily averages for the PM<sub>2.5</sub> measurements with the APM2 optical method and the APM filter sampling as reference method from the St. Petersburg. The orthogonal

regression analysis between the site analyzer APM optical method against the APM filter sampling as reference method according to the GDE is shown in Figure 4.21.

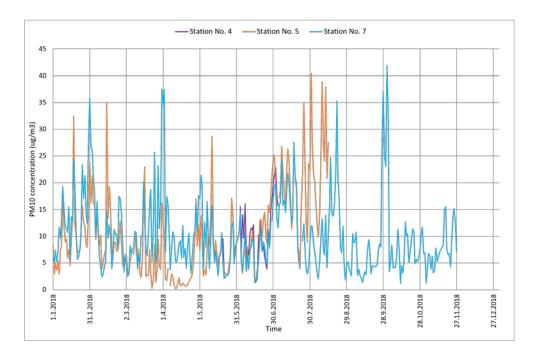


**Figure 4.20.** The daily average values of PM<sub>2.5</sub> mass concentration for site analyzer APM2 optical method and the APM2 filter method as the reference method at station No. 4 in St. Petersburg.

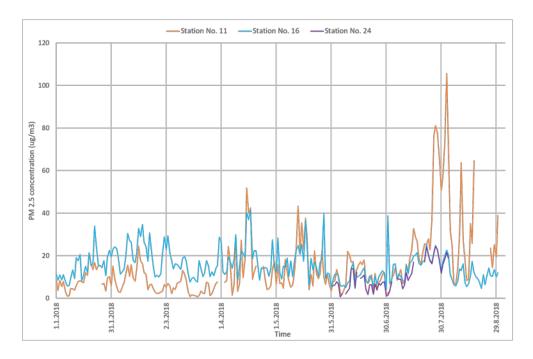


**Figure 4.21.** Orthogonal regression analysis between the APM optical method and the APM filter sampling as reference method for PM<sub>2.5</sub>, see text in Figure 4.3 except that in the figure right the slope is not forced through the origin.

The time series of local  $PM_{10}$  measurements in St. Petersburg at stations No. 4, No. 5 and No. 7 are shown in Figure 4.22 and  $PM_{2.5}$  measurements at stations No. 11, No. 16 and No. 24 in Figure 4.23.



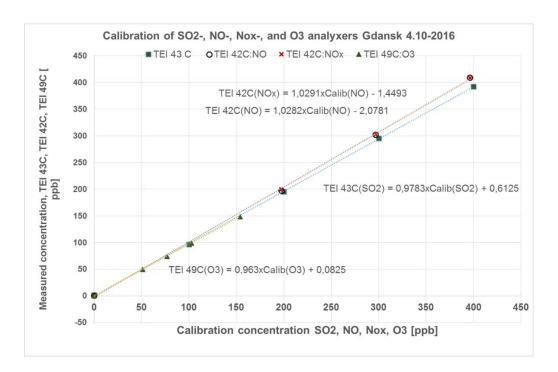
**Figure 4.22.** The daily average values of  $PM_{10}$  concentration at stations No. 4, No. 5 and No. 7 in 2018.



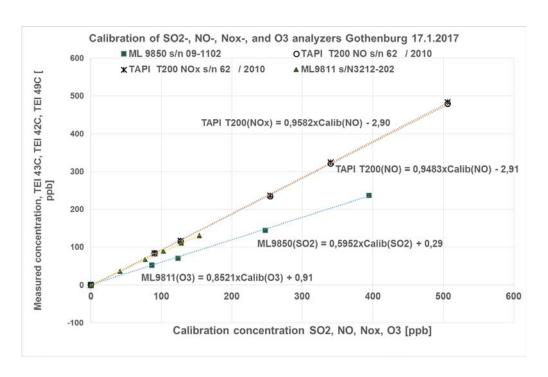
**Figure 4.23.** The daily average values of  $PM_{2.5}$  concentration at stations No. 11, No. 16 and No. 24 in January–August 2018.

## 4.4 Gaseous air pollution from Gdansk, Gothenburg and St. Petersburg

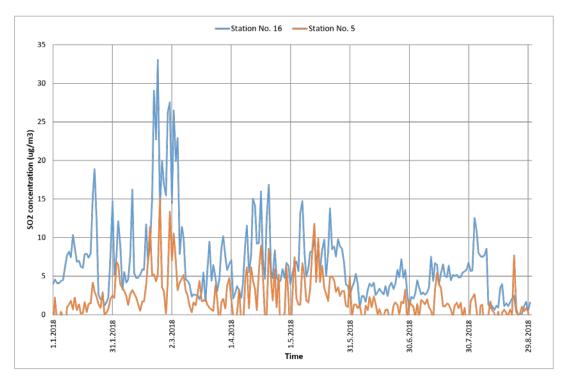
Calibration results of the  $SO_2$ ,  $NO-NO_x$  and  $O_3$  analyzers at station AM8 in Gdansk are presented in Figure 4.24. CO measurements were not conducted at station AM8 and therefore no CO calibration was made. In Figure 4.25, the calibration results of the  $SO_2$ ,  $NO-NO_x$  and  $O_3$  analyzers at station Femman in Gothenburg are presented. As mentioned earlier, calibrations of gas analyzers in St. Petersburg were not able to conduct. Instead, the time series of local  $SO_2$  and  $NO_2$  measurements in St. Petersburg are investigated at stations No. 5, No. 7, No. 11 and No. 16 (Figures 4.26 and 4.27, respectively).



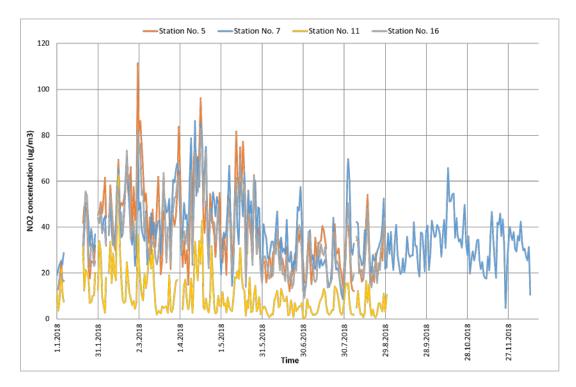
**Figure 4.24.** Calibration of the  $SO_2$ , NO and  $O_3$  analyzers at station AM8 in Gdansk. The calibration concentrations are shown in x-axis while the output concentrations of the station analyzers are in y-axis. The regression equations for each of the analyzers are shown in the figure beside the regression lines.



**Figure 4.25.** Calibration of the  $SO_2$ , NO and  $O_3$  analyzers at station Femman in Gothenburg. The calibration concentrations are shown in x-axis while the output concentrations of the station analyzers are shown in y-axis. The regression equations for each of the analyzers are shown in the figure beside the regression lines.



**Figure 4.26.** The daily average values of  $SO_2$  concentration at stations No. 5 and No. 16 in St. Petersburg in January–August 2018.



**Figure 4.27.** The daily average values of  $NO_2$  concentration at stations No. 5, No. 7, No. 11 and No. 16 in St. Petersburg in 2018.

## 4.5 Summary of comparison and calibration results in Gdansk, Gothenburg and St. Petersburg

Summary of the comparison results of the measurements of particulate matter for  $PM_{10}$  and  $PM_{2.5}$  as well as calibration of analyzers are collected in Table 4.2. Correction equation presented in Table 4.2 is the inverse function of the regression equation from the analysis of the comparison measurements.

**Table 4.2.** Calibration equations (slope and the intercept) to correct the site analyzers either for particulate matter for  $PM_{10}$  and  $PM_{2.5}$  or for gaseous compounds and their estimated uncertainty at pilot cities of Gdansk, Gothenburg and St. Petersburg. ND means not defined, e.g., comparison measurement was not conducted or analysis was not conducted.

Measurement quantity	Gdansk			Gothenburg			St. Petersburg		
	Slope	Intercept	Expanded uncertainty	Slope	Intercept	Expanded uncertainty	Slope	Intercept	Expanded uncertainty
PM10	1,227y		13,8 %	0,962y		13,3 %	1,712y		40,2 %
PM2.5	1,864y		31,7 %	ND		ND	0,694y		69,7 %
NO	0,973	2,021	11.9 %	1,055	3,069	ND	ND	ND	ND
Nox	0,972	1,408	11.9 %	1,044	3,027	ND	ND	ND	ND
SO2	1,022	-0,626	9.7 %	1,680	-0,487	ND	ND	ND	ND
О3	1,038	-0,086	9.7 %	1,174	-1,068	ND	ND	ND	ND

## 4.6 System audits from pilot cities

The questionnaires of the audits, listed in Annex 2-4 separately for each measurement network, present the results of the audit. Here, the main findings are summarized.

For gas measurements, compliance with EN standards (EN 14211, EN 14212, EN 14625, EN 14626) was assessed for all cities even though in Russia, these standards are not in use and national standards apply. In all cities continuous analyzers were used. The quality control procedures in gas measurements were on a good level. All the measurements were calibrated. Some minor shortages regarding cleaning of sampling parts, calibration frequency, span checks and documentation were found. Measurement uncertainty was calculated for most measurements, or the process of calculating was on-going during the audit.

In Gdansk and Gothenburg, automated measurement systems (AMS) were used while in St. Petersburg a reference method with automatic filter sampling was used. For PM measurements with AMS, there was no EN standard available at the time of the audit. Since then, EN 16450 describing the PM measurements for automated measurement systems has been published but it is not yet included in the EU air quality legislation. During the audit, the draft version of the EN standard was available and

compliance of PM measurements was evaluated on that basis even though full compliance in Gdansk and Gothenburg could not be expected due to lack of standardization and legislation requirements. The PM measurements in St. Petersburg were assessed according to requirements in EN 12341 for PM reference methods.

The quality control of AMS measurements followed partly the EN draft version. Frequency of calibrations of flow and sensors was adequate, however, checks between calibrations were missing. According to EN 16450, these instruments need to be tested for equivalence against the reference methods to be accepted. Intercomparisons between the AMS and the reference method had been conducted in Gdansk and Gothenburg, however, the usage of calibration factors was omitted. The PM measurements in St. Petersburg were mainly following EN 12341.

Level of documentation (e.g., standard operation procedures (SOPs) for measurements, data validation and other activities, calibration and maintenance plans, registers, log books, Quality Manual) was good in the accredited networks. In Gothenburg, only the most essential measurement activities were documented. Personnel being audited were all experts with good experience in air quality measurements.

During the audits, no activities causing erroneous results were detected for gas measurements. For PM measurements, the main concern was the lack of usage of calibration factors for the continuous analyzers. This topic is addressed in Chapter 4.1 where the PM comparison results are presented.

### **Summary**

The air quality measurements in Europe are conducted to reach knowledge on the level of concentrations of air pollutants in order to demonstrate the effect of abatement strategies and to know the health effects on people based on the exposure of pollutants into human beings. Comparability of the measurement results between the air quality measurements across the Europe is therefore most important and lot of efforts has been put in legislation, standardization, quality systems, reference laboratories and their accreditation, defining the reference methods, interlaboratory comparisons, traceability of measurements and estimation of uncertainty of measurement results. In this study we conduct the comparison study for particulate matter and gaseous compounds in the pilot cities of the project to reach the comparability of the measurements within the study area. The quality management system (QMS) of the network in the pilot cities was audited in order to demonstrate the existence and functioning of the QMS as well as to check if the QA/QC procedures conducted in the field follows the requirements set up in the relevant EN-standards.

The comparison studies at pilot cities for particulate matter and gaseous compounds were part of the activities in work package 3.3 within the EnviSuM project. The main goal was to harmonize the different measurement methods conducted at air quality measurements at the pilot cities around the Baltic Sea region. The output of the comparison results was intended to adjust the model results and the measured data at the three pilot cities in the project. The comparison method and the analysis of the results follows the guideline providing the EC. In case of measurements of particulate matter, the comparison did not fulfill the requirements for the demonstration of equivalence of particle instrument against the reference method regarding to the number of field campaigns and the duplicate instrumentations, it give a short verification for the performance of the PM instruments used at the local air quality sites/network.

In the ARMAAG network in the city of Gdansk, both PM<sub>10</sub> and PM<sub>2.5</sub> measurements were conducted at station AM8. In case of PM<sub>10</sub> the agreement between the site analyzer, Eberline 62-I, and the reference method was fairly good with the use of correction factor. To correct the original results with a slope correction makes the correction slightly easy especially for low concentration and would increase the

uncertainty of results slightly compared to the case where correction is used for the slope and the intercept, see, e.g., Figure 4.3. In case of PM2.5 the performance of the TEOM 1400ab is not very good as shown in Figure 4.7. The scatter of results is considerable large causing the uncertainty for the correction outside the acceptable limit.

In the network of the city of Gothenburg, there was only  $PM_{10}$  measurements at Gårda station where the comparison took place. However also  $PM_{2.5}$  measurements were conducted with the reference method and with the optical method (Grimm 180). The signal from the site analyzer for  $PM_{10}$ , TEOM 1400ab, was corrected with two factors (see in Table 4.1): first the original signal is corrected for the slope and intercept (Original signal = 1.19x signal + 1.15 ( $\mu$ g/m3)) and secondly, to estimate the amount of semi-volatile fraction in the air factor of -1.87xTEOM(VCM) was used for additional correction as described in 3.2. In spite of the corrections obtained to TEOM 1400ab, the orthogonal regression analysis propose to correct the results for the slope as shown in Table 4.1. Correction can be made either by correcting the results with the slope and intercept with expanded uncertainty of 13.6% or by correcting the results with the slope resulting slightly lower uncertainty of 9.6%. The IVL sampler pass the orthogonal regression analysis without any correction factors with the expanded uncertainty of 10.7%. The results of Grimm 180 are acceptable without any correction but the uncertainty decreases when addition correction is made for the slope and intercept or for the slope only. Since the limit for the expanded uncertainty is 25%, we can state that all three PM instruments pass the tests thus TEOM1400ab and IVL sampler with lower uncertainty value than Grimm 180.

In St. Petersburg, the comparison for particulate matter was modified from the practice conducted in Gdansk and in Gothenburg as mentioned earlier. The network analyzer for particulate matter, APM-analyzer which MINERAL uses both for  $PM_{10}$  and  $PM_{2.5}$  measurements is equipped with optical method and for filter sampling method. The filter sampling method was used as a reference method and the optical method as a site analyzer against which the comparison was conducted. The performance of the APM optical method was not acceptable both for  $PM_{10}$  and  $PM_{2.5}$  measurements. The uncertainty of the APM optical method exceed the allowed uncertainty for fixed measurements as stated by Air Quality Directive, see in Table 4.2. Instead the APM passed the tests for indicative measurements where the uncertainty of the measurements should not exceed 50%. It was surprising, however that the slope differed very much between  $PM_{10}$  and  $PM_{2.5}$  measurements, as shown in Table 4.2.

The results of calibration of the air quality analyzers for gaseous compounds succeeded extremely well at ARMAAG network in city of Gdansk, as shown in Figure 4.22. Good result was also detected in case of  $NO-NO_x$  and  $O_3$  measurements, but not for  $SO_2$  measurements in the city of Gothenburg.

The purpose of the station and quality management system (QMS) audits was to demonstrate existence of the QMS and whether it was used. We checked if the QA/QC procedures defined by the relevant ENstandards for the reference method were respected at the measurement sites.

It turned out that in Tricity the QMS by ARMAAG was accredited according to EN ISO/IEC 17025 standard for the field measurements of gaseous compounds (but not for particulate matter). In general, the QMS was well-documented, including the plans for calibration and maintenance of the equipment. The QA/QC activities followed the requirements by the EN standards. A few nonconformities were observed during the audit survey and were reported to the network responsibilities.

Gothenburg maintained the QMS that covered the activities in the field and fulfilled the requirements by the EN-standards. The QMS used was a "light version" of a quality management system with some documentation, such as instructions, logbooks and calendars, but the network does not have a Quality Manual and it does not utilize EN ISO/IEC 17025.

In St. Petersburg, the QMS maintained by SC-MINERAL followed the requirements of the national legislation and national standards. It includes defined QA/QC activities for field measurements that were similar but not exactly the same as those defined by EN standards.

At each network the traceability of measurement results were arranged to the national or international standards as required by the Air Quality Directive (AQD).

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Demonstration of Equivalence of Ambient Air Monitoring Methods, 2005. EC-working group on guidance for the demonstration on equivalence) (http://ec.europa.eu/environment/air/quality/legislation/pdf/equivalence.pdf)

EN 12341:2014 Ambient air — Standard gravimetric measurement method for the determination of the  $PM_{10}$  or  $PM_{2,5}$  mass concentration of suspended particulate matter

EN 14211:2012. Ambient air – Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence.

EN 14212:2012. Ambient air – Standard method for the measurement of the concentration of sulphur dioxide by UV fluorescence.

EN 14625:2012. Ambient air – Standard method for the measurement of the concentration of ozone by ultraviolet photometry.

EN 16450:2017. Ambient air – Automated measuring systems for the measurement of the concentration of particulate matter (PM10; PM2.5).

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Waldén J., Waldén T., Laurila S., Hakola H., 2017. Demonstration of the equivalence of PM<sub>2.5</sub> and PM<sub>10</sub> measurement methods in Kuopio 2014–2015. Finnish Meteorological Institute, Reports 2017:1, 134 pp., Helsinki.

### Annex 1. Protocol for conducting the comparison studies in EnviSuM project

#### WP3. Comparison of air quality measurement:

The target of the intercomparison and audit study is to

- achieve the comparability of air quality measurement results within the air quality measurement sites that are involved with the EnviSuM project,
- demonstrate that the networks are conducting the QA/QC procedures at the site according to the relevant EN standards,
- help to assess the effect of the new legislation and to evaluate the model results of Tasks 3.2.

The cities that are included into the comparison are:

- · Gothenburgh in Sweden,
- The Tricity (Gdansk, Sopot and Gdynia) in Poland, and
- St. Petersburg in Russia

The comparison scheme consist of visit to sites for a period of 2 month/each sites. The activities includes

- 1. calibration of the air quality instruments for gaseous compounds with the calibration facility by FMI at the beginning and end of the comparison.
- 2. the comparison of the station analyzers for  $PM_{10}$  and  $PM_{2.5}$  against the reference method defined by the Directive 1480/EU/2015 and described in EN 12341:2014 as well as in EN 16450:2017. The comparison of both size class is conducted simultaneously. The target is to achieve > 40 samples/class size.
- 3. the audit for the quality system of the network

Gases and PM: NO, SO<sub>2</sub>, CO, O<sub>3</sub>, PM<sub>10</sub> & PM<sub>2.5</sub>

Equipment: PM<sub>10</sub>/PM2.5 samplers: Leckel SEQ-47-50, sequential PM reference sampler

Continuous PM analyzer: Grimm 180 (PM<sub>10</sub>-PM<sub>2.5</sub>-PM<sub>1</sub>)

Dilution device: Teledyne T700: Calibration ranges:

-NO: 0 - 500 ppb Gas standard: NO in N<sub>2</sub>: C = 20 ppm;  $U=\pm 1\%$ 

-SO<sub>2</sub>: 0 - 250 ppb Gas standard: SO<sub>2</sub> in N<sub>2</sub>: C = 10 ppm;  $U = \pm 1\%$ 

-CO: 0 - 10 ppm Gas standard: CO in Synthetic air: C = 1000 ppm;  $U=\pm 1\%$ 

Gas standards: NO, SO<sub>2</sub>, CO

Calibrator: ozone 0 – 200 ppb

Flow measurement device



### **Dimensions**

Width 482 mm

Depth 310 mm

Height with inlet 1.585 m

## Weight

approx. 60 kg (transportable by casters)

### Operation of Leckel samplers:

FMI provides the sampling filters for comparison. The comparison period is 8 weeks. Weighing of the filters is conducted at the FMI according to the EN 12341:2014 and accredited according to EN ISO/IEC 17025:2005.

- FMI brings two sets of filter cartridges for both of the samplers. The cartridges includes 14 sampling filters and a blank filter covering the time of 14 days.
- After a period of 4 weeks FMI brings another sets of filters for the next 4 weeks period. The first sampling filters from the cartridges are removed into the petrislides and are brought back to FMI for weighing. The new filters are then packed into the cartridges, the ones installed directly in the samplers (PM<sub>10</sub> & PM<sub>2.5</sub>) and the others left for the change after 2 weeks.
- Detail procedure from the beginning of the PM sampling:
- Installation of the samplers and the filter cartridge
- Two weeks from beginning: First set of filter sampling is past and the filter cartridge should be replaced with a new filter cartridge. The sampled filter cartridge should be stored in a cool storage (temperature between 5 and 10 °C, if possible). The change of filter cartridge should be made by staff of MINERAL after given instruction.
- Four weeks from beginning: FMI brings new sets of filter (pre-weighted). The sampled filters are
  removed from the cartridges into the petri slides to return them to FMI for weighing. The new
  filters will be loaded into the cartridges for the next sampling periods. The sampling inlets are
  cleaned and the impaction plate is greased by FMI.
- Six weeks from beginning: MINERAL will change the sampled filter cartridge with the last set of filter cartridge and will store them in a storage.
- Eight weeks from beginning: FMI collects the sampled filters into the petri slides. Sampling equipment are packed to transport back to Finland.

### Calibration of the gas analyzers:

- FMI will bring T400 gas dilutor
- Flow measurement system
- Ozone calibrator
- Gas standards from VNIIM: CO (2000 ppm), NO (10/50 ppm) and SO2 (10/50 ppm)
- Tubings

### MINERAL:

- Zero air generator
- Pressure regulators for gas standards from VNIIM
- Calibration of the station analyzers, beginning of the campaign and at the end of the campaign:
- Installation of the calibration facilities at the site(s)
- Conduct the calibration: SO<sub>2</sub> range: 0 250 ppb
- NO: 0 500 ppb
- CO: 0 10 ppm
- O<sub>3</sub>: 0 200 ppb

# Annex 2. Equivalent test results

### **TEOM 1400ab**

**Table A1a.** Results from the orthogonal regression analysis of TEOM 1400ab at Gårda against the reference method. Correction with the slope and intercept.

		GENER#	AL SETTINGS		
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	μg/m <sup>3</sup>	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
		DATA S	SELECTION		
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	TEOM 1400 ab+VCN			
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter				Ignore
Filter 4	Study	EnviSum			Active
		CALIBRAT	TION SETTING		
Calibration based on:	SLOPE AND	DINTERCEPT		OK	
				UK	
RAN	V DATA		RESULTS A	FTER CALIBRATING	
Regression	0,941y + 0,82		N (Spring)	0	n
Regression (i=0)	0,961y		N (Summer)	0	n
N	50	n	N (Fall)	0	n
			N (Winter)	50	n
Outliers	2	n	Outliers	0	n
Outliers	4,0	%	Outliers	0,0	%
Mean CM	29,89	μg/m3	Mean CM	28,94	μg/m3
Mean RM	28,94	μg/m3	Mean RM	28,94	μg/m3
Number of RM > UAT	15	n	Number of CM > UAT	17	n
Number of RM > LV	5	n	Number of CM > LV	4	n
	RESULTS (RAW)			ESULTS (CALIBRATED)	
Slope b	1,0628	significant	Slope b	0,9990	
Uncertainty of b	0,0274		Uncertainty of b	0,0258	
Intercept a	-0,8718		Intercept a	0,0289	
Uncertainty of a	0,9152		Uncertainty of a	0,8611	
r^2	0,968		r^2	0,968	
Slope b forced through origin	1,040	significant			
Uncertainty of b (forced)	0,0135				
EQUIVALEN	CE TEST (RAW)		EQUIVALENCI	TEST (CALIBRATED)	
Uncertainty of calibration	1,649	μg/m3	Calibration	(y+0,872) / 1,063	
Uncertainty of calibration (forced)	0,676	μg/m3	Uncertainty of calibration	1,649	μg/m3
Random term	3,1597	µg/m3	Random term	3,3909	µg/m3
Additional uncertainty (optional)	0,00	μg/m3	Additional uncertainty (optional)	0,00	μg/m3
Bias at LV	2,2692	μg/m3	Bias at LV	-0,0210	μg/m3
Combined uncertainty	3,8901	μg/m3	Combined uncertainty	3,3909	μg/m3
Expanded relative uncertainty	15,5604%	pass	Expanded relative uncertainty	13,5637%	pass
Ref sampler uncertainty	0,6700	μg/m3	Ref sampler uncertainty	0,6700	μg/m3
Limit value	50	μg/m3	Limit value	50	μg/m3
			L INFORMATION		
		Raw data,	free intercept		
dxdy	dyy	dxx	rss	uat	u(b)
14338	15474	13726	501	30	0,027
		Raw data, slope	forced through origin		
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
57585	60135	55604		0,013	0,014
		Calibrated	, free intercept		
dxdy	dyy	dxx	rss		u(b)
13491	13699	13726	443		0,026
		BACKGROU	ND AUTOMATION		
Chart descriptions	3	Confi.Lvl List	Calibration List	Stdev of all calibrations	s in use
Description x-axis	RM PM10 Leckel 4	97,5%		0	0,01352
Description y-axis	CM PM10 TEOM 1	97,5%	Free regression		5151515
Confi.Lvl	Calibration Type	Filter List	Through origin	Calib. In use (a)	Calib. In use (b)
2,31	-2	Exclude		0,872	1,063
Calibration uncertainty	Calibration_a	Calibration_b	u(bs_reference)	CI Regression	Cl Calibrated
1,649	0,872	1,063	0,6700	7,47	8,39

**Table A1b.** Results from the orthogonal regression analysis of TEOM 1400ab at Gårda against the reference method. Correction is made for the slope, forced through the origin.

GENERAL SETTINGS					
Substance	Unit	Limit value	DM upsortainty	Confidence Lavel	May Upcortainty
	µg/m <sup>3</sup>		RM uncertainty	Confidence Level	Max Uncertainty
PM10		50 Summer	0,67 Fall	0,975 Winter	25 %
Starting month:	Spring 3	6	9	12	
DATA SELECTION	3	0	9	12	
DATA SELECTION	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	EOM 1400 ab+VC			Active
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter	OK			Active
Filter 4	Study				Ignore
CALIBRATION SETTING	,				3
Calibration based on:	DPE TROUGH ORI	SIN	OK		
RAW DATA			RESULTS AFTER CALIBRATING		
Regression	1,001y + -0,833		N (Spring)	0	n
Regression (i=0)	0,98y		N (Summer)	0	n
N	50	n	N (Fall)	0	n
			N (Winter)	50	n
Outliers	2	n	Outliers	2	n
Outliers	4,0	%	Outliers	4,0	%
Mean CM	29,11	μg/m3	Mean CM	28,52	µg/m3
Mean RM	28,31	μg/m3	Mean RM	28,31	µg/m3
Number of RM > UAT	14	n	Number of CM > UAT	16	n
Number of RM > LV	5	n	Number of CM > LV	5	n
REGRESSION RESULTS (RAW)			REGRESSION RESULTS (CALIBRATEI		
Slope b	0,9988		Slope b	0,9783	
Uncertainty of b	0,0222		Uncertainty of b	0,0218	
Intercept a	0,8322		Intercept a	0,8222	
Uncertainty of a	0,7314		Uncertainty of a	0,7165	
r^2	0,976		r^2	0,976	
Slope b forced through origin	1,021	significant			
Uncertainty of b (forced)	0,0115				
EQUIVALENCE TEST (RAW)			EQUIVALENCE TEST (CALIBRATED)		
Uncertainty of calibration	1,330	μg/m3	Calibration	(y+0,000) / 1,021	
Uncertainty of calibration (forced)	0,575	μg/m3	Uncertainty of calibration	0,575	µg/m3
Random term	2,5557	μg/m3	Random term	2,5653	µg/m3
Additional uncertainty (optional)	0,00	μg/m3	Additional uncertainty (optional)	0,00	µg/m3
Bias at LV	0,7703	μg/m3	Bias at LV	-0,2635	µg/m3
Combined uncertainty	2,6693	µg/m3	Combined uncertainty	2,5788	µg/m3
Expanded relative uncertainty	10,6772%	pass	Expanded relative uncertainty	10,3152%	pass
Ref sampler uncertainty	0,6700	μg/m3	Ref sampler uncertainty	0,6700	µg/m3
Limit value	50	µg/m3	Limit value	50	µg/m3
STATISTICAL INFORMATION					
Raw data, free intercept	dest	dun			
dxdy	dyy	dxx	rss	uat	u(b)
13860	14010	14045	335	30	0,022
Raw data, slope forced through origi		0		u/b\fMaul-ilia1 : 0	u/b famadi
Sxy	Syy	SXX		u(b)[MaxLike] i=0	u(b_forced)
55075 Calibrated, free intercept	56386	54131		0,011	0,012
	dana	dust	roo		LL/b)
dxdy 13570	dyy 13448	dxx 14045	rss 322		u(b) 0,022
13579 BACKGROUND AUTOMATION	10446	14045	322		0,022
		Confi Lyl List	Calibration List	Stdey of all-palibrations	in use
Chart descriptions	DM DM40 Lookel 4	Confi.LvI List	Cambration List	Stdev of all calibrations	
Description x-axis Description y-axis	RM PM 10 Leckel 4	**********	Eroo regression	0	0,01150
Confi.Lvl	CM PM 10 IVL- sam Calibration Type		Free regression	Calib. In use (a)	Calib. In use (b)
2,31	-1	Filter List Exclude	Through origin	0.000	1,021
Calibration uncertainty	Calibration_a	Calibration b	u(bs reference)	CI Regression	CI Calibrated
0,575	1,021	1,021	0.6700	6,11	6,25
0,070	1,021	1,021	0,0700	0,11	0,20

**Table A2.** Results from the orthogonal regression analysis of IVL sampler at Gårda against the reference method. No further correction is needed.

					-
Culti ottorio	Linit		RAL SETTINGS	Confidence	May I have the
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	μg/m³	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
			SELECTION		
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	IVL-PM10 sampl			Active
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter	OK			Active
Filter 4	Study				Ignore
			ATION SETTING		
Calibration based on:	SLOPE AND	NTERCEPT		OK	
7.00			27011170		
RAW				FTER CALIBRATING	
Regression	1,001y + -0,833		N (Spring)	0	n
Regression (i=0)	0,98y		N (Summer)	0	n
N	50	n	N (Fall)	0	n
0.11			N (Winter)	50	n
Outliers	2	n o	Outliers	1	n
Outliers	4,0	%	Outliers	2,0	%
Mean CM	29,11	μg/m3	Mean CM	28,31	μg/m3
Mean RM	28,31	μg/m3	Mean RM	28,31	μg/m3
Number of RM > UAT	14	n ~	Number of CM > UAT	16	n
Number of RM > LV	5	n	Number of CM > LV	5 (COLUMN TO (CALUDE ATER)	n
REGRESSION R				ESULTS (CALIBRATED)	
Slope b	0,9988		Slope b	1,0000	
Uncertainty of b	0,0222		Uncertainty of b	0,0223	
Intercept a	0,8322		Intercept a	-0,0004	
Uncertainty of a	0,7314		Uncertainty of a	0,7323	
r^2	0,976		r^2	0,976	
Slope b forced through origin	1,021	significant			
Uncertainty of b (forced)	0,0115				
EQUIVALENCE				TEST (CALIBRATED)	
Uncertainty of calibration	1,330	μg/m3	Calibration	(y-0,832) / 0,999	
Uncertainty of calibration (forced)	0,575	μg/m3	Uncertainty of calibration	1,330	μg/m3
Random term	2,5557	μg/m3	Random term	2,8843	μg/m3
Additional uncertainty (optional)	0,00	μg/m3	Additional uncertainty (optional)	0,00	μg/m3
Bias at LV	0,7703	μg/m3	Bias at LV	0,0003	μg/m3
Combined uncertainty	2,6693	μg/m3	Combined uncertainty	2,8843	µg/m3
Expanded relative uncertainty	10,6772%	pass	Expanded relative uncertainty	11,5372%	pass
Ref sampler uncertainty	0,6700	μg/m3	Ref sampler uncertainty	0,6700	μg/m3
Limit value	50	μg/m3	Limit value	50	μg/m3
		STATISTIC	AL INFORMATION		
		Raw data	a, free intercept		
dxdy	dyy	dxx	rss	uat	u(b)
13860	14010	14045	335	30	0,022
		Raw data, slope	e forced through origin		
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	
55075	56386	54131		0,011	0,012
		Calibrate	ed, free intercept		
dxdy	dyy	dxx	rss		u(b)
13877	14045	14045	336		0,022
		BACKGROU	UND AUTOMATION		
		Confi.Lvl List	Calibration List	Stdev of all calibrations	in use
Chart descriptions					CONTRACTOR
Chart descriptions  Description x-axis	RM PM10 Leckel 47	97,5%		0	0,01150
		97,5% 97,5%	Free regression	0	0,01150
Description x-axis	RM PM10 Leckel 47		Free regression Through origin	0  Calib. In use (a)	0,01150  Calib. In use (b)
Description x-axis Description y-axis	RM PM10 Leckel 4: CM PM10 IVL-PM1 Calibration Type -2	97,5%			
Description x-axis Description y-axis Confi.Lvl	RM PM10 Leckel 47 CM PM10 IVL-PM1 Calibration Type	97,5% Filter List		Calib. In use (a)	Calib. In use (b)

**Table A3a.** Results from the orthogonal regression analysis of Grimm 180 at Gårda against the reference method. Correction with the slope and intercept.

		OFNE	AL OFTINGS		
Substance	Unit	Limit value	RAL SETTINGS  RM uncertainty	Confidence Level	Max Uncertainty
PM10	µg/m <sup>3</sup>	50	0,67	0,975	25 %
1 10110	Spring	Summer	Fall	Winter	25 /6
Starting month:	3	6	9	12	
			SELECTION		
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	Grimm 180			Active
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter	OK			Active
Filter 4	Study	EnviSum			Active
	_	CALIBRA	ATION SETTING		
Calibration based on:	SLOPE AND	INTERCEPT		ОК	
	DATA			TER CALIBRATING	
Regression	1,05y + 1,666		N (Spring)	0	n
Regression (i=0)	1,102y		N (Summer)	0	n
N	50	n	N (Fall)	0	n
Outliers	0	n	N (Winter) Outliers	50	n n
Outliers	0,0	n %	Outliers	0.0	
Mean CM	24,24	μg/m3	Mean CM	27,11	μg/m3
Mean RM	27,11	μg/m3	Mean RM	27,11	μg/m3
Number of RM > UAT	13	n	Number of CM > UAT	15	n
Number of RM > LV	4	n	Number of CM > LV	6	n
REGRESSION I	RESULTS (RAW)		REGRESSION RI	ESULTS (CALIBRATED)	
Slope b	0,9524		Slope b	1,0027	
Uncertainty of b	0,0442		Uncertainty of b	0,0464	
Intercept a	-1,5869		Intercept a	-0,0737	
Uncertainty of a	1,3691		Uncertainty of a	1,4375	
r^2	0,897		r^2	0,897	
Slope b forced through origin	0,907	significant			
Uncertainty of b (forced)	0,0212				
	E TEST (RAW)			TEST (CALIBRATED)	
Uncertainty of calibration	2,600	μg/m3	Calibration	(y+1,587) / 0,952	
Uncertainty of calibration (forced)	1,058	μg/m3	Uncertainty of calibration	2,600	μg/m3
Random term Additional uncertainty (optional)	4,6917 0.00	μg/m3 μg/m3	Random term Additional uncertainty (optional)	5,5799 0.00	μg/m3 μg/m3
Bias at LV	-3,9656	μg/m3	Bias at LV	0,0622	μg/m3
Combined uncertainty	6,1432	μg/m3	Combined uncertainty	5,5803	μg/m3
Expanded relative uncertainty	24,5726%	pass	Expanded relative uncertainty	22,3211%	pass
Ref sampler uncertainty	0.6700	μg/m3	Ref sampler uncertainty		μg/m3
Limit value	50	μg/m3 μg/m3	Limit value	0,6700 50	μg/m3
Littit value	30		AL INFORMATION	30	ру/110
			a, free intercept		
dxdy	dvy	dxx	rss	uat	u(b)
10151	10234	11224	1078	30	0,044
.0101			e forced through origin		5,011
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
43009	39605	47981		0,021	0,021
		Calibrate	ed, free intercept		
dxdy	dyy	dxx	rss		u(b)
10658	11282	11224	1192		0,046
			UND AUTOMATION		
Chart descriptions		Confi.Lvl List	Calibration List	Stdev of all calibrations	
Description x-axis	RM PM10 Leckel 47			0	0,02117
Description y-axis	CM PM10 Grimm 1	97,5%	Free regression		
Confi.LvI	Calibration Type	Filter List	Through origin	Calib. In use (a)	Calib. In use (b)
2,31	-999	Exclude		1,587	0,952
Calibration uncertainty	Calibration_a	Calibration_b	u(bs_reference)	CI Regression	CI Calibrated
2,600	1,000	1,000	0,6700	10,96	12,50

**Table A3b.** Results from the orthogonal regression analysis of Grimm 180 at Gårda against the reference method. Correction with the slope, forced through the origin.

		OFNE	AL CETTINGS		
Substance	Unit	Limit value	RAL SETTINGS  RM uncertainty	Confidence Level	Max Uncertainty
PM10	μg/m <sup>3</sup>	50	0,67	0,975	25 %
1 10110	Spring	Summer	Fall	Winter	25 /0
Starting month:	3	6	9	12	
		DATA	SELECTION		
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	Grimm 180			Active
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter	OK			Active
Filter 4	Study	EnviSum			Active
			ATION SETTING		
Calibration based on:	SLOPE TROU	JGH ORIGIN		ОК	
DAW	DATA		DECLUTE A		
	DATA			FTER CALIBRATING	
Regression	1,05y + 1,666		N (Spring)	0	n
Regression (i=0)	<b>1,102y</b> 50		N (Summer)	0	n
TV	30	n	N (Fall) N (Winter)	50	n n
Outliers	0	n	Outliers	0	n n
Outliers	0,0	%	Outliers	0,0	%
Mean CM	24,24	μg/m3	Mean CM	26,71	μg/m3
Mean RM	27,11	µg/m3	Mean RM	27,11	µg/m3
Number of RM > UAT	13	n	Number of CM > UAT	15	n
Number of RM > LV	4	n	Number of CM > LV	6	n
	RESULTS (RAW)			ESULTS (CALIBRATED)	
Slope b	0,9524		Slope b	1,0554	
Uncertainty of b	0,0442		Uncertainty of b	0,0487	
Intercept a	-1,5869		Intercept a	-1,9035	
Uncertainty of a r^2	1,3691 0,897		Uncertainty of a r^2	1,5089 0,897	
Slope b forced through origin	0,897	significant	1,5	0,897	
Uncertainty of b (forced)	0,0212	Significant			
· /	E TEST (RAW)		FOLIIVAI ENCE	E TEST (CALIBRATED)	
Uncertainty of calibration	2,600	µg/m3	Calibration	(y+0,000) / 0,907	
Uncertainty of calibration (forced)	1,058	μg/m3	Uncertainty of calibration	1,058	μg/m3
Random term	4,6917	μg/m3	Random term	5,3011	μg/m3
Additional uncertainty (optional)	0,00	μg/m3	Additional uncertainty (optional)	0,00	μg/m3
Bias at LV	-3,9656	μg/m3	Bias at LV	0,8654	μg/m3
Combined uncertainty	6,1432	μg/m3	Combined uncertainty	5,3713	μg/m3
Expanded relative uncertainty	24,5726%	pass	Expanded relative uncertainty	21,4851%	pass
Ref sampler uncertainty	0,6700	μg/m3	Ref sampler uncertainty	0,6700	μg/m3
Limit value	50	μg/m3	Limit value	50	μg/m3
		STATISTIC	CAL INFORMATION		
			a, free intercept		
dxdy	dyy	dxx	rss	uat	u(b)
10151	10234	11224	1078	30	0,044
			e forced through origin	(-\1)	(1- (- 1)
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
43009	39605	47981	ed, free intercept	0,021	0,021
dxdy	dvy	dxx			u(b)
11188	12430	11224	rss 1317		0,049
11100	12400		UND AUTOMATION		0,040
Chart description	s	Confi.Lvl List	Calibration List	Stdev of all calibrations	s in use
Description x-axis	RM PM10 Leckel 47			0	0,02117
Description y-axis	CM PM10 Grimm 1	97,5%	Free regression		
		Filter List	Through origin	Calib. In use (a)	Calib. In use (b)
Confi.LvI	Calibration Type	I IIICI LISI		Callo. Ill acc (a)	
2,31	Calibration Type -1	Exclude	THE GGIT GITGHT	0,000	0,907
			u(bs_reference) 0,6700	1717	

**Table A3c.** Results from the orthogonal regression analysis of APM optical method at St. Petersburg against the APM filter sampling as reference method. Correction with the slope and intercept.

		GENERAL	SETTINGS		
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	μg/m <sup>3</sup>	50		0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
		DATA S	ELECTION		
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM Instrument	PNS16D-APM			Active
Filter 2	RM Instrument	Derenda 16D sampler	•		Active
Filter 3	Orientation	OK			Active
Filter 4					Ignore
			ION SETTING		
Calibration based on:	SLOPE AND	INTERCEPT		OK	
	W 5474		25011 70 4		
	AW DATA			FTER CALIBRATING	
Regression	1,3y + 6,791		N (Spring)	0	n
Regression (i=0)	1,712y	_	N (Summer)	48	n
IN	48	n	N (Fall) N (Winter)	0	n
Outliers	0	n	Outliers	0	n n
Outliers	0.0	n %	Outliers	0.0	%
Mean CM	14,03	μg/m3	Mean CM	25,03	μg/m3
Mean RM	25.03	µg/m3	Mean RM	25,03	μg/m3
Number of RM > UAT	12	n	Number of CM > UAT	15	n
Number of RM > LV	1	n	Number of CM > LV	1	n n
	N RESULTS (RAW)			RESULTS (CALIBRATED)	
Slope b	0,7690	significant	Slope b	1,1108	
Uncertainty of b	0,0859	<b>3</b>	Uncertainty of b	0,1117	
Intercept a	-5,2226	significant	Intercept a	-2,7723	
Uncertainty of a	2,3100	<b>3</b>	Uncertainty of a	3,0038	
r^2	0,506		r^2	0,506	
Slope b forced through origin	0,584	significant			
Uncertainty of b (forced)	0,0311				
EQUIVALE	NCE TEST (RAW)		EQUIVALENC	E TEST (CALIBRATED)	
Uncertainty of calibration	4,877	μg/m3	Calibration	(y+5,223) / 0,769	
Uncertainty of calibration (forced)	1,556	μg/m3	Uncertainty of calibration	4,877	μg/m3
Random term	6,0907	μg/m3	Random term	9,6582	µg/m3
Additional uncertainty (optional)	0,00	μg/m3	Additional uncertainty (optional)	0,00	µg/m3
Bias at LV	-16,7701	μg/m3	Bias at LV	2,7659	μg/m3
Combined uncertainty	17,8419	μg/m3	Combined uncertainty	10,0465	µg/m3
Expanded relative uncertainty	71,3675%	fail	Expanded relative uncertainty	40,1859%	fail
Ref sampler uncertainty	0,6700	μg/m3	Ref sampler uncertainty	0,6700	μg/m3
Limit value	50	μg/m3	Limit value	50	µg/m3
			. INFORMATION		
			free intercept		
dxdy	dyy	dxx	rss	uat	u(b)
2739	3192	4647	1727	30	0,086
0			orced through origin	(-).[\\.]1.:	/h
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
19589	12634	34716	free intercent	0,031	0,031
dydy	day	- Cambratoa,	noo mioroopi		14/b)
dxdy 3562	dyy 5397	dxx 4647	rss 3218		u(b) 0,112
3302	5581		D AUTOMATION		U, IIZ
Chart description	10	Confi.Lvl List	Calibration List	Stdev of all calibrations	in use
Description x-axis	RM PM10;Derenda 1	97,5%	Calibration List	0	0,03112
Description x-axis  Description y-axis	CM PM10; Derenda 1		Free regression	U	0,03112
Confi.Lvl	Calibration Type	Filter List	Through origin	Calib. In use (a)	Calib. In use (b)
2,32	-2	Exclude	Through origin	5,223	0,769
Calibration uncertainty	Calibration_a	Calibration_b	u(bs_reference)	CI Regression	CI Calibrated
4,877	5,223	0,769	0,0000	14,19	18,13
		0,700	0,0000	17,10	10,10

# Annex 3. System audit reports



### **SYSTEM AUDIT REPORT**

### Auditor:

Katriina Kyllönen, Quality Manager Finnish Meteorological Institute Research and Development/Air Quality Research P.O. 503 FI-00100 Helsinki Finland katriina.kyllonen@fmi.fi

P. +358 50 352 6722 Fax: +358 9 19295403



#### **SYSTEM AUDIT REPORT**

(P) Measurement station: ARMAAG, AM8, Gdansk

(P) Location: Gdańsk - Wrzeszcz, ul. Leczkowa

Raporteur: Katriina Kyllönen

Representatives: Michalina Bielawska (assistant of quality manager), Tomek Kotakowski and

Michal Sarafin (technicians)

Date of audit: 31.10.2016

#### 1. Measurement station

### a: Site classification: Urban background

Purpose of the measurements: The station is part of the national air quality network in Poland and has been established for monitoring the air quality in Gdansk. The compliance with limit values is followed. Air quality reports are prepared and information for the public provided. The measurement of gases (NO-NO<sub>2</sub>-NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>3</sub>) have been accredited according to EN ISO/IEC 17025:2005 since 2009.

#### Measurement components:

- NO-NO<sub>2</sub>-NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>3</sub>, PM<sub>10</sub> & PM<sub>2.5</sub> with US/EPA heads The measurement methods for gas components are those described in the relevant ENstandards i.e. EN14211 for NO-NO<sub>2</sub>, EN14212 for SO<sub>2</sub>, EN14625 for O<sub>3</sub>, EN14626 for CO, and for particulate matter EN12341 and CEN/TS 16450 for PM<sub>10</sub> and PM<sub>2.5</sub>.
- At the station, following instruments are also maintained: Calibrator Thermo Dynamic gas calibrator system Model 146 and zero air MCZ Air Purifier K15
- Meteorological instrumentation: speed and wind direction, humidity, temperature, precipitation and pressure
- Major hazard component:

Measurement activities started: October 1998

#### b: Description of the station:

Located in the side of an open area with a large parking lot and playing field. There were only two cars at the parking lot at the time of audit. A busy road is close to the station (some tens of meters), car frequency 26 000 cars per day (street Gen. Józefa Hallera).



The station is fenced in, locked and secured against interferences. The roof has no railings, but can be accessed with ladder kept at the station.

Fire extinguisher was found at the station but no first aid kit was installed.

Photos around the station:









c: Environmental conditions: During the audit: cloudy, temperature 8 °C, low wind speed

**d: Overview of the station:** See maps below for map of Gdansk and map of station surroundings. The station is marked with red circle (maps: Google Maps).







### 2. Personnel of the station

Tomek Kotakowski, Michal Sarafin and Tomasz Waszczyk (technicians)

Responsible person: Michal Sarafin

### 3. Sampling line

### Sampling manifold:



a: Description of the manifold: An L-shaped manifold, diameter 5 cm (estimated); not heated.

**b: Material:** Borosilicate glass, with Teflon tube ahead of the manifold



- c: Length of the manifold: 1 m above container roof, 1.5 m inside the cabin, not insulated.
- d: Flow rate inside the manifold: Not known.
- **e:** Check of the sampling line: Sample lines are changed every 8-10 years and cleaned when visible dirt is observed (this applies to the sample line part prior to filter holder). *EN standards*: Sampling lines shall be changed or cleaned at least every six months.
- **f: Testing of the manifold:** The sample manifold is cleaned every 6 months. The testing is not performed by the station technicians but by the Chief Inspectorate for Environmental Protection / National Reference Laboratory / National Network (not accredited, hereafter referred as national reference laboratory). Leak test and efficiency tests with test gases are then performed simultaneously for sample manifold and sample line. The testing is performed every three years and last time performed in September 2016. The report was not available at the time of the audit.

### 4. Analyzers:





### a: Analysers:

- NOx, Thermo 42 C
- SO2, Thermo 43 C
- CO, Thermo 48C
- O3, Thermo 49C
- PM10, Eberline FH 62-1
- PM2.5, MLU TEOM 1400A
- US/EPA heads
- Calibrators: Thermo Dynamic gas calibrator system Model 146 for SO2, NOx and CO. The span check and calibration are conducted with the same instrumentation. In addition, the network has an ozone calibrator Thermo 49C-62618-336 placed at another station at the time of audit.
- Zero gas: MCZ Air Purifier K15
- The measurement methods for gas components are those described in the relevant ENstandards i.e. EN14211 for NO-NO<sub>2</sub>, EN14212 for SO<sub>2</sub>, EN14625 for O<sub>3</sub>, EN14626 for CO, and for particulate matter EN12341 for PM<sub>10</sub> and PM<sub>2.5</sub>.

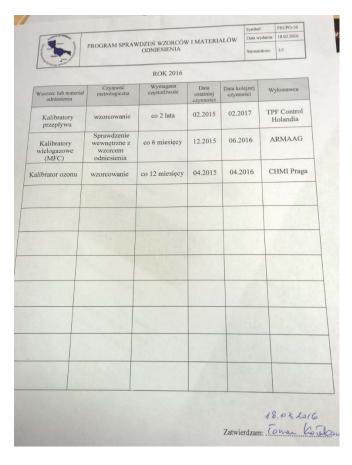






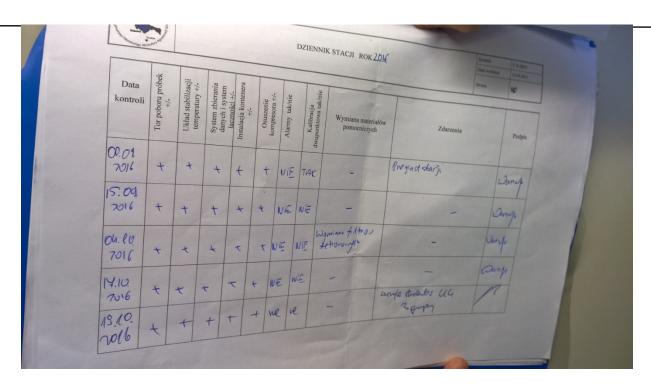
### 5. Maintenance and calibrations

a: Maintenance and calibration plan? Calibration plan, available at the office, see photo below.



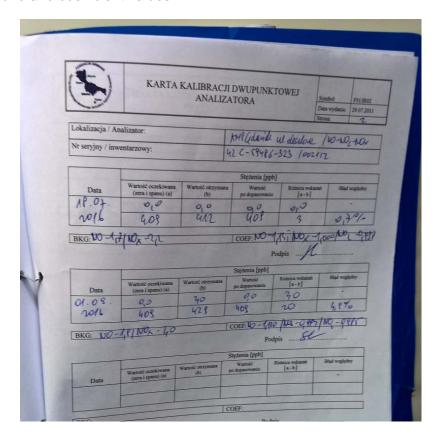
- b: Are there written SOPs for maintenance, calibrations? Yes, in Polish.
- **c:** Frequency of the maintenance of the analyser: Less than 3 weeks.
- **d: Actions during the maintenance:** The maintenance logbook (maintained both in a printed and electronic form) has the following information (see photo below):
  - Date and signature
  - Check of manifold and sample line
  - Check of temperature at the station
  - Check of data logger and acquisition, connection to server
  - Check of container conditions
  - Check of dry compressor
  - Check of alarms of the analysers
  - Performance of two-point calibration (yes/no)
  - Change of consumables, e.g. filters
  - Special activities and notes





The calibration logbook contains the following information (see photo below):

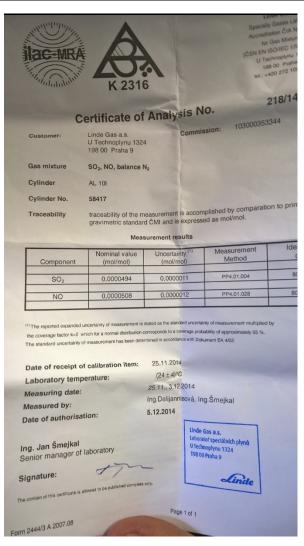
- Date
- Measured and theoretical values of zero and span
- Values after adjustment
- Differences (both absolute and percentage) to theoretical value
- Background and coefficient values

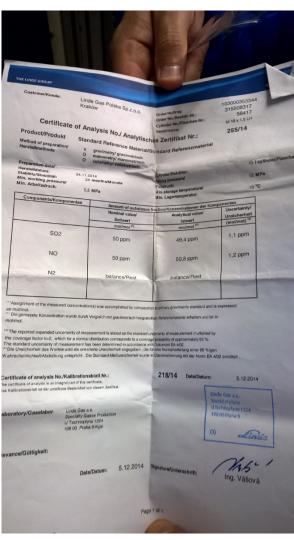




- e: Change of the particulate filter: Performed when the filter is visibly dirty, typically once a month but at least every three months. Particulate filter material is Teflon (Millipore 4.5 µm pore size). Filter housing material is Teflon. Filter housing is cleaned twice a year, last time September 2016 (not clearly documented: logbook "technical check" covers for a wide variety of actions).
- **f: Zero and span checks: method and frequency:** With the calibrator at the site (Thermo Dynamic gas calibrator system and MCZ Air Purifier K15). Performed automatically every 71 h.
- **g: Concentration of Span:** Span concentrations for analysers: 400 ppb (SO2 and NO), 4 ppm (CO).

Gas	Cylinder	Certificate	Nominal	Analyzed	Exp	Date of	Date of expir
standard		nr			uncertainty	analysis	
CO in N2	2741500	6292/D-K- 14146-01-00	-	495 ppm	± 1 % (rel.)	11.12.2015	12/2018
NO in N2	58417	255/14	50 ppm	50.8 ppm	1.2 ppm	24.11.2014	-
SO2 in N2	58417	255/14	50 ppm	49.4 ppm	1.1 ppm	24.11.2014	-

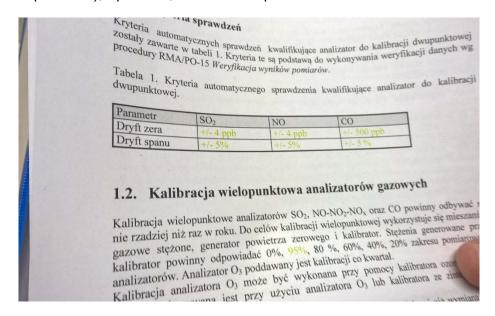








h: Action criteria for zero and span: According to EN standards, Zero:  $\leq$  -4 or  $\geq$  4 nmol/mol (CO: -0.5 or 0.5 µmol/mol), Span:  $\geq$  5,0 % of initial span value. See SOP below.





- i: Check of field (span) standard: The field standards are compared at installation with the previous standards. After that, they are not checked but considered valid until the end of the certificate date unless earlier disqualified for improper performance. EN standards: The stability of the gases used for span and zero checks shall be verified at least every six months with use of reference gases traceable to (inter)nationally accepted standards. These gases shall fulfil the specifications in Table 1.
- **j: Frequency of the calibration:** Calibration is conducted with the same system as span checks. At least every three months and always after exceedance of span and zero criteria. The last three calibrations have been performed in 18.7.2016, 1.9.2016 and 15.9.2016 (the last calibration performed by the national reference laboratory, others by the network). Two-point calibration is employed. Once in every two years, the national reference laboratory performs multipoint calibration at the sites with their own calibration systems. This was last done in September 2016 but the report has not been delivered yet.
- **k:** Check of linearity: Once a year for SO2, NOx and CO, four times a year for O3. Documentation was not assessed.
- **I:** Check of converter efficiency (NO-NOx analyser): Once a year. Last time in 1.9.2016. Documentation was not assessed.
- m: Traceability of calibration standards (ISO 17025; 5.6) :

The ozone calibrator is traceable to NIST USA SRP 17 (CHMI, Prague, Czech republic).

The traceability of the other gases is managed by Linde Gas a.s., Specialty Gases Laboratory, accredited for gas mixtures by EN ISO/IEC 17025:2005. In the certificates, traceability is described as following:

- SO2 and NOx: Traceability of the measurement is accomplished by comparation to primary gravimetric standard CMI and is expressed as mol/mol.
- CO: Assignment of the measured concentration was accomplished by comparation to primary gravimetric standard and is expressed as mol/mol.

The network takes part in intercomparisons organized by the national reference laboratory annually. This is a requirement of accreditation.

- n: Where does the traceability of the calibration standards lead: As described above.
- o: How often the field calibration equipment/facility is calibrated against the reference standard (e.g. in the calibration laboratory): Span gas cylinders are not calibrated (see 5.i).
- **p:** Estimation of the expanded uncertainty of the field measurements (5.4.6): Technician Tomek Kotakowski is in charge of measurement uncertainty calculations that are performed with excel sheets prepared by him. Measurement uncertainties are given below.

SO2	9.7 %
NO-NO2-NOx	11.9 %
O3	9.7 %
CO	11.1 %
PM10	25 %
PM2.5	25 %



### 6. Zero gas

- a: Means of preparation of zero gas at the station: Internal zero air purifier (MCZ Air Purifier K15).
- b: How often the scrubbing materials are changed inside the zero air generator: Once a year.

#### 7. PM measurements



- a: QA/QC procedures conducted for the measurements, see in Table 2. At the site, there are no log books for PM measurements and no SOPs have been prepared. The measurement is not accredited. While there are no documentation available, in practice, PM measurements are otherwise treated as the gas measurements.
  - The operational parameters are manually checked twice a day at the office (start of day, at noon)
  - Calibration of sensors for temperatures, pressure and humidity is performed once a year. No checks are done in-between. <u>FprEN 16450 standard</u>: Where temperature, pressure (difference) and/or relative humidity sensors are essential to assure the accuracy of the PM mass concentration measurement made by the instrument, these shall be checked using appropriate transfer standards with readings traceable to (inter)nationally accepted standards. These checks shall be performed before the flow rate check. Minimum frequency every three months, please, see NOTE 8.4.4.
  - Calibration of the AMS flow rates are done once a year. No checks are done in-between. <u>FprEN 16450 standard</u>: Checks of instantaneous flow rates shall be performed using an appropriate flow meter with readings traceable to (inter)nationally accepted standards. Minimum frequency every three months.
  - Leak check of the sampling system is performed once a year.
  - Zero and span calibration is performed by foil every six months.
  - Some checks and regular maintenance of components of the AMS measuring system are performed when needed, e.g. change of tape, check of the pump.

**b:** How often the sampling inlet is cleaned and how? The impactor plate of the sampling inlet is cleaned by wiping off the dirty grease and applying new grease twice a year. In addition, the plate is sometimes rotated without the change of grease. The sampling inlet is not cleaned otherwise. See photo of the inlets below. *EN standard:* Sample inlets shall be cleaned and impaction plates cleaned and greased according to the manufacturer's requirements, taking into account local particulate concentrations. If no instructions on cleaning/greasing intervals are given by the manufacturer, the impaction plates shall be greased at least every 30th sample for PM10 and 15th sample for PM2.5; depending on the PM concentration.



c: Do you crease the impactor plate of the inlet: US-EPA inlet. See above.

d: Demonstration of equivalence with the reference method: A few years ago, an intercomparison with the reference method was organized. The network was supplied with the data from the reference method. The network made the data analysis and recovered a correction factor of 1.21. This factor is not applied for the data. The reference method was still employed at the site.

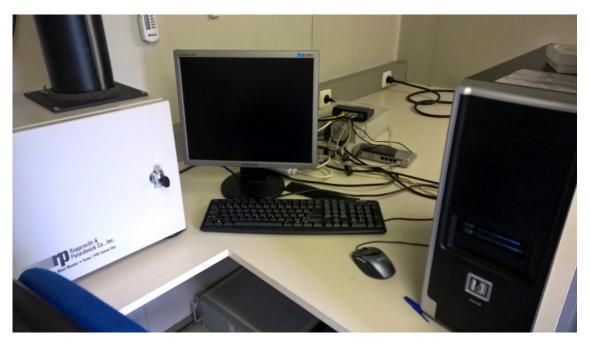
### 8. Data collection

a: Data acquisition system: ENVIRO

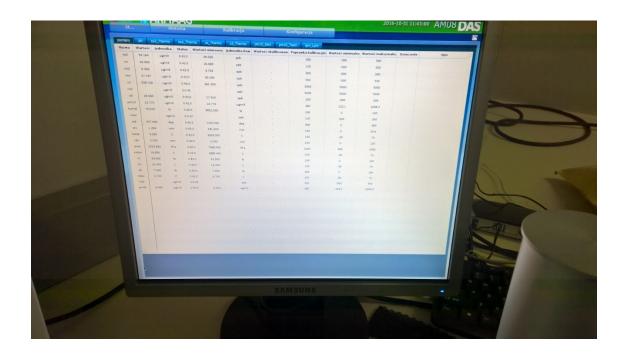
**b:** How the data is sent to central data collection server: Every 10 seconds by cable.

c: Data validation routine?

Automatic checks are performed on the data by the local station software. The data is color coded with five different colors. White data is considered valid (data coverage is at least 75 %), while the other colors stand for e.g. calibration, incorrect automatic calibration, no data, or incomplete or abnormal data. Manual checks are applied at two stages, the initial verification and the proper verification. Initial verification is done twice daily on working days and is conducted to observe any abnormalities at the station or with the data, e.g. technical problems, automatic calibration errors, extreme values, rapid changes in data, lack of data etc. Proper verification is performed prior to the acceptance of the data according to SOP (RMA/PO-15 Verification of the measurement results).







### e: Is there any QA/QC procedures for data validation and reporting?

Yes, for data validation there is a SOP titled RMA/PO-15 *Verification of the measurement results*. Proper verification is performed once a month. In addition, a yearly verification is performed after the end of the calendar year.

For reporting, there is a SOP titled RMA/PO-02 *Co-operation with the customer*. Two kinds of reports are prepared, monthly and yearly reports, and they include also opinions and interpretation of the data.

#### 9. Documentation

### a: Are there logbooks for the measurements and maintenance at the station?

The logbook is maintained as a duplicate in electronic and manual written form stored at the site, please, see 5d for details.

### b: Does anyone check the log books?

Since the technicians are also taking part in data verification, the information in logbooks is not at risk to be ignored.

### c: Where do the manuals of the equipment locate?

At the site, summaries about the relevant procedures are maintained as paper copies. The summaries have been prepared by the technicians in Polish. Original manuals in English and Polish are stored in the office.



### 10. Audits

**a:** Have there been any external audits and if by whom? An accreditation assessment with lead and technical assessors is conducted once a year.

### 11. Quality System (QS), Reference to ISO 17025

- a: Does the QS include the station activities? If so reference to SOP. Yes, the measurements at the station are accredited and described in SOPs (see 11d).
- **b:** How is the QS implemented at the station? The measurements of gases are accredited. There are several SOPs that include activities performed at the station. The calibration program is shown in 5.a. An internal audit is performed at the station every second year.
- **c:** Are the relevant SOPs available at the station? Yes, paper copies are stored at the site.
- d: Check and comments of the SOPs relevant to AQ measurements at the site.

All the SOPs are in Polish so no comments are given. See list of SOPs below.

- <u>e:</u> Complains (4.8) Treatment of complains is stated in the Quality manual and a separate SOP. There is a register for complaints (not assessed).
- <u>f:</u> Improvements (4.9) Treatment of improvements is stated in the Quality manual and a separate SOP. Improvements are made e.g. according to suggestions of internal audits and accreditation assessments.
- **g:** Corrective actions (4.9) Treatment of corrective actions is stated in the Quality manual and a separate SOP. There is a register for corrective actions (not assessed).
- <u>h:</u> Internal audits (4.14) Internal audits are performed annually including documentation and activities at the site. In addition, an annual management review is organized.
- <u>i:</u> Personnel (5.2) There is a separate SOP for training. The personnel interviewed during the audit have all M.Sc. degrees in relevant fields (geography, meteorology, climatology, and chemical and environmental protection).

#### **List of SOPs:**

General instructions (freely translated titles from Polish)

- 1. Supervision and management of procedures (document control)
- 2. Co-operation with customers
- 3. Supervision of complaints
- 4. Delivery and service (purchasing services and supplies)
- 5. Control of nonconforming testing work
- 6. Improvements

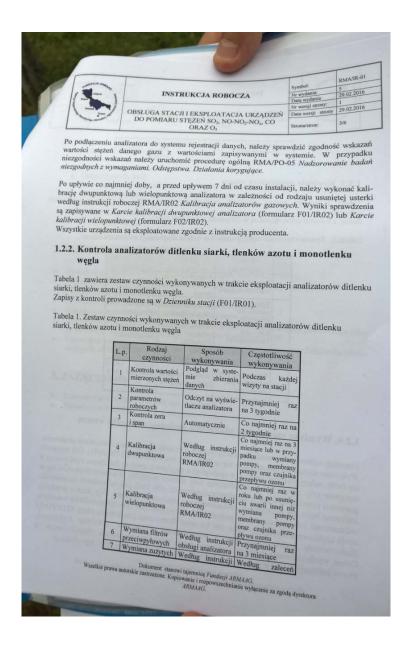


- 7. Internal audits
- 8. Training
- Management review
- 10. Quality management system assuring the quality. Internal QC procedures and calibration
- 11. Validation and measurement uncertainty
- 12. Verification of the measurement results
- 13. Protection of data
- 14. Equipment (how to purchase and control)

### **Technical instructions**

- 1. Management of the activities at the station (SO2, NO-NO2-NOx, CO and O3)
- 2. Calibration of gas analysers (see photo below)
- 3. Checking mass flow controllers

(For PM measurements, there are no written SOPs for technical instructions.)





### **Comments and recommendations (summary):**

The measurements of gases (but not PM) are accredited according to EN ISO/IEC 17025:2005 and annually assessed by the official accreditation body. The network has a very good documentation system at the office. The documentation of procedures at the site could be slightly improved (e.g. the procedures performed, such as cleaning of the parts, could be clearly specified in the log book) and PM measurements should be documented in the same manner as gas measurements. Some remarks about following the EN standards are given in the report *in italic* concerning nonconformities of QA/QC procedures for gases and PM.



Table 1. The checks and calibrations together with their frequency; gas measurements

Calibration, checks and maintenance	Frequency	Action criteria
Calibration of the analyser	At least every three months and after repair	
Certfifcation of test gases	At least every six months	Zero: ≥ detection limit  Span: ≥ 5,0 % from last certified value
Zero and span check	At least every two weeks	Zero: $\leq$ -4 or $\geq$ 4 nmol/mol (CO: -0.5 or 0.5 µmol/mol) Span: $\geq$ 5,0 % of initial span value
Repeatability at zero and span of the analyser	In combination with calibration, using the data from the calibration	Repeatability standard deviation at zero: 1.0 nmol/mol (NO), 5.0 nmol/mol (SO2), 1.5nmol/mol (O3), 0.5 µmol/mol (CO)  Repeatability standard deviation at span: 0.75% (NO), 1.5 % (SO2), 2% (O3), 3% (CO)
Lack of fit check (to be performed in laboratory or in field)	Within 1 year after installation and after repair; further frequency depending on the result of test	lack of fit > 4,0 % of the measured value lack of fit > 5 nmol/mol at zero (CO: 0.5 μmol/mol)
Converter efficiency (NO)	At least every year	≤ 95 %
Testing sample manifold -influence of pressure drop induced by the manifold pump - sample collection efficiency	At least every three years	influence > 1 % of measured value (pressure drop; 9.6.3/4.1)



		influence > 2 % of the measured value (sample collection efficiency; 9.6.3/4.2)
Change of particulate filters c of the sampling system at the sampling inlet and/or at the analyser inlet	Depending on the results of a test as prescribed in 9.3, but at least every three months	Response to span gas passing the filter is ≤ 97 %
Test of the sampling lines	At least every six months	≥ 2 % sample loss
Changing of (if applicable): drying material and other consumables	At least every six months	As required
Regular maintenance of components of the analyser	As required by manufacturer	As required

a Span value: recommended concentration of 70 % to 80 % of the certification range for NO2 or 70 % to 80 % of the certification range of NO, depending on which check gas is used.

- b Recommended every 23 h or 25 h.
- c The particulate filter shall be changed periodically depending on the dust loading at the sampling site. During this filter change the filter housing shall be cleaned. Overloading of the particulate filter may change the concentration of nitrogen monoxide and/or nitrogen dioxide.
- d Dependent on site-specific conditions.
- e If infringement of an action criterion occurs, corrective actions shall be taken as soon as possible. An evaluation of the influence of the detected infringement on the measurement data produced before the actual correction of the infringement took place shall be given and taken into account during data validation. To ensure that the data capture criterion is met, data will need to be inspected by a trained operator every working day.
- f This requirement differs from the requirement in the type approval laboratory test. In this laboratory test the converter is new and therefore the requirement is more stringent and set at ≥ 98 %.

Table 2. QA/QC procedures for the automated PM analyzers

Calibration, checks and maintenance	Clause	Minimum Frequency <sup>a</sup>	Lab/ field	Action criteria <sup>b</sup>	Uncertainty requirements for transfer standards
Checks of status values of operational parameters (see 7.5.4)	8.4.3	Daily (on working days)	L/F	See below	
Checks of sensors for temperatures, pressure and/or humidity <sup>c</sup>	8.4.4	Every 3 months	F	± 2 °C ± 1 kPa ± 5 % RH	
Calibration of sensors for temperatures, pressure and/or humidity <sup>c</sup>	8.4.5	Every year	L/F		1,5 °C 0,5 kPa 3 % RH
Check of the AMS flow rate(s)	8.4.6	Every 3 months	F	±5%	2 %
Calibration of the AMS flow rate(s)	8.4.7	Every year	L/F		1 %
Leak check of the sampling system	8.4.8	Every year	F	±2%	
Zero check of the AMS reading	8.4.9	Every year	L/F	± 3 μg/m³	
Check of the AMS mass measuring system	8.4.10	As recommended by the manufacturer and after repair, but at least every year	L/F	as set out by manufacturer, or ± 3% if necessary	
Regular maintenance of components of the AMS	8.5	As required by the manufacturer	L/F	as set out by manufacturer	

<sup>&</sup>lt;sup>a</sup> Frequencies of checks and calibrations may be relaxed when sufficient history exists demonstrating that drifts of sensor readings and flow rates remain within the specified requirements.

b With reference to nominal values.

<sup>&</sup>lt;sup>c</sup> For some instruments such checks and calibrations are not possible in situ because of the positioning of the sensors within the AMS. Therefore, these checks and calibrations are restricted to sensors that are accessible in the field (typically in the sampling head). As a part of the annual checks, the checks may be performed in a laboratory room with constant temperature and relative humidity by comparing sensor readings (after stabilization) with those of reference standards.



## **SYSTEM AUDIT REPORT**

## Auditor:

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## SYSTEM AUDIT REPORT

Measurement stations: Two stations Femman and Gårda in the Gothenburg city centre

**Locations:** (1) Femman, address Nordstaden (on the roof of the shopping center, 27 m high)

(2) Gårda, address Tritongatan (by the street, 4m high)

Raporteur: Katriina Kyllönen

Representatives: Emma Björkman

Date of audit: 15.2.2017

## 1. Measurement station

a: Site classification: Urban background / Femman, traffic station / Gårda

Purpose of the measurements: The station is part of the national air quality network in Sweden and has been established for monitoring the air quality in Gothenburg. The measurements are conducted by Gothenburg city (Miljöförvaltningen). The compliance with limit values is followed at Femman. Air quality reports are prepared and information for the public provided (web: http://goteborg.se/wps/portal/start/miljo/miljolaget-i-goteborg/luft/luften-just-nu/!ut/p/z1/04\_Sj9CPykssy0xPLMnMz0vMAfljo8ziAwy9Ai2cDB0N\_N0t3Qw8Q7wD3Py8ffydnQz1w wkpiAJKG-AAjgb6BbmhigDFKUNa/dz/d5/L2dBISEvZ0FBIS9nQSEh/)

Measurement components, Femman:

- NO<sub>x</sub>, SO<sub>2</sub>, O<sub>3</sub>, PM<sub>10</sub> & PM<sub>2.5</sub> with US/EPA heads

  The measurement methods for gas components are those described in the relevant ENstandards i.e. EN14211 for NO-NO<sub>2</sub>, EN14212 for SO<sub>2</sub>, EN14625 for O<sub>3</sub>, and for particulate matter EN12341. CEN/TS 16450 for PM<sub>10</sub> and PM<sub>2.5</sub> is not used by the network. Currently, CO has not been measured by the network since the instrument broke down in 2016. However, the network did employ EN14626 for CO. Buying a new monitor is under consideration at the moment.
- At the station, following instruments are also maintained by the network: Gas calibrator with zero air cylinders
- Meteorological instrumentation: speed and wind direction, humidity, temperature, precipitation, solar irradiation and pressure
- In addition, precipitation samples are collected for chemical analysis and IVL measures VOCs with GC at the station.
- Major hazard component:



## Measurement components, Gårda:

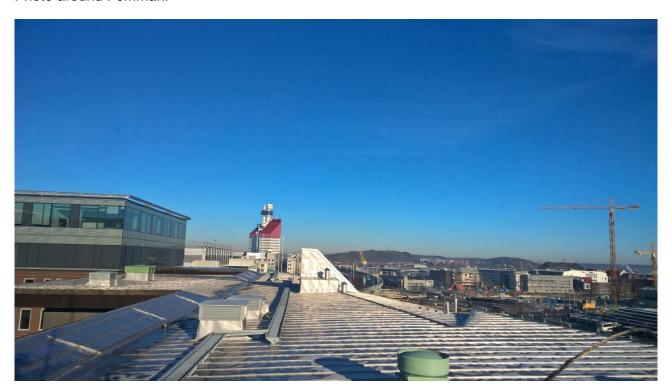
- NO<sub>x</sub>, PM<sub>10</sub> with US/EPA heads
   The measurement methods for gas components are those described in the relevant EN-standards i.e. EN14211 for NO-NO<sub>2</sub> and EN12341 for PM<sub>10</sub>.
- At the station, following instruments are also maintained: Calibrator for NOx (with zero air cylinders attached)
- Meteorological instrumentation: speed and wind direction, temperature
- Major hazard component:

Measurement activities started: At Femman, the measurements started first with NOx measurements in 1976 and other gases were included in the measurement program later on. PM measurements were started in 1990. At Gårda, NOx and PM measurements were started in 1996 and 2004, respectively.

## b: Description of the station:

Femman is located in the centre of Gothenburg on the rooftop of a shopping mall Nordstan. The measurements are performed at a height of about 30 m. The building is surrounded by roads. The station facilities are located in the top floor (7<sup>th</sup>) of the mall with access to the mall roof by ladders where the inlets for sampling are located on a small sampling terrace. The station is locked and secured against interferences. Fire extinguisher and a first aid kit are stored at the station.

#### Photo around Femman:

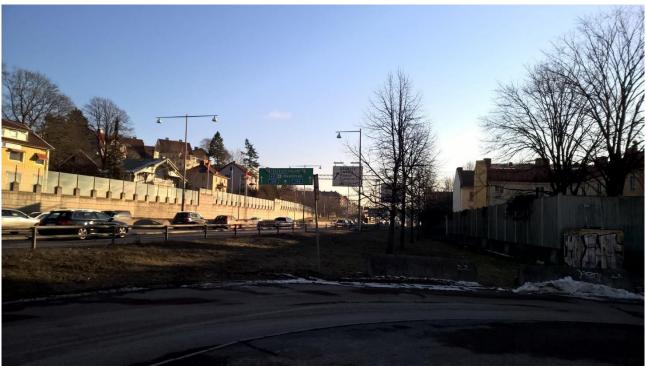




Gårda is located in a parking lot less than 2 km southwest of Femman. A busy motorway Kungsbackaleden/E6 with seven traffic lanes is next to the station (less than 10 meters), car frequency 100 000 cars per day of which 9 % is heavy traffic. Driving speed limit is 70 km/h. The station is located more than 25 m away from the closest major crossroad (CAFÉ directive requirement). The NOx instrument is located inside a concrete stand of an overpass while the PM10 instrument is placed outside in a small cabin with fences around it. The station is locked.

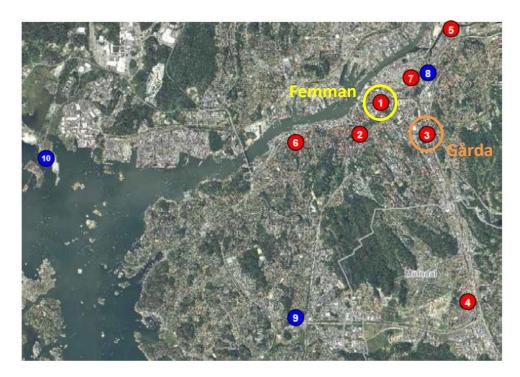
Photo of and around Gårda:





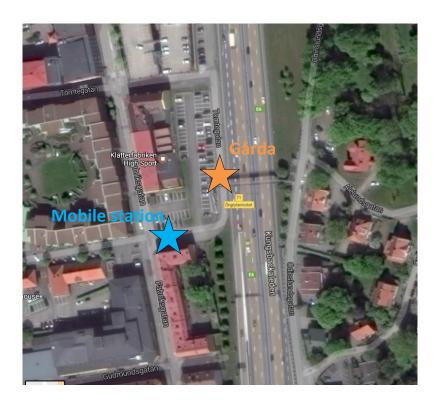


- c: Environmental conditions: During the audit: sunny, temperature about 5 °C, low wind speed
- **d: Overview of the station:** See below for map of Gothenburg and the measurement stations in the city. The red stations are for air quality and blue stations for meteorology (map: Göteborgs stad, Miljöförvaltning). In addition, maps of station surroundings are given below (maps: Google Maps). One of the mobile stations was located next to Gårda and was shortly visited (not part of audit).









This audit report describes the activities mostly at Femman, but the same principles apply at Gårda. If measurements at Gårda are described in the report, the station name is clearly mentioned.



## 2. Personnel of the station

Names and responsibilities:

Hung Nguyen: Instruments at Femman, data analysis and validation, reporting to Swedish EPA, responsible person for Femman.

Emma Björkman: NOx measurements, calibrations, measurement uncertainties, written air quality reports, responsible person for Gårda and deputy for Femman.

Helene Olofsson: Measurement uncertainties, written air quality reports, responsible person for Haga and mobil station no 2.

Erik Svensson: PM measurements, deputy responsible person for Gårda, responsible person for mobil station no 1 and 3.

## 3. Sampling line

## Sampling manifold and line:



**a: Description of the manifold:** An L-shaped manifold, diameter about 15 and 7 cm (estimated); not heated at Femman. At Gårda, no manifold is needed since only one gas monitor is maintained at the station. The sampling line is routed into a metal cage with a rain shield attached at Gårda.

**b: Material:** Glass (likely borosilicate made by Humi-glas)



- **c:** Length of the manifold: 1 m (estimated) inside the cabin, sample tube 3 m (estimated) above container roof, not insulated.
- d: Flow rate inside the manifold: Not known. Pump is attached to the end of the manifold.
- **e:** Check of the sampling line: Sample lines (Teflon) are changed every 6 months and thus EN standards followed.
- **f: Testing of the manifold:** The sample manifold is cleaned every 12 months. The date for the last change was not available at the station.

No leak test or efficiency tests with test gases are performed.

## 4. Analyzers:





## a: Analysers:

- The measurement methods for gas components are those described in the relevant ENstandards i.e. EN14211 for NO-NO<sub>2</sub>, EN14212 for SO<sub>2</sub>, EN14625 for O<sub>3</sub>, and EN12341 for PM<sub>10</sub> and PM<sub>2.5</sub>.

### Station Gårda

- NOx, Thermo Scientific 42i
- PM10, TEOM 1400 AB with US/EPA head
- No gas calibrator at the site. The NOx monitor is calibrated with a gas cylinder tested at Femman before use.

## Station Femman

- NOx, Teledyne T200
- SO2, Ecotech 9850B
- O3, Monitorlabs ML 9811
- PM10 and PM2.5, TEOM 1405 DF with US/EPA heads
- Calibrator and zero gas, Ecotech GasCal 1100

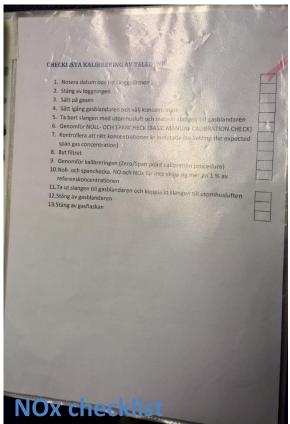
## 5. Maintenance and calibrations

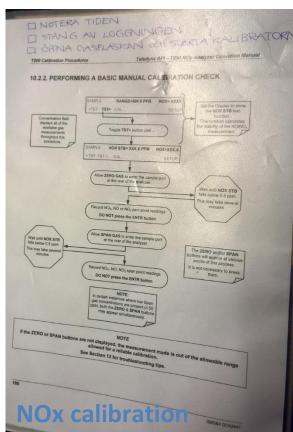
**a: Maintenance and calibration plan?** Maintenance plan was maintained at the station in printed form (see photo below). No official calibration plan is maintained but calibration is mentioned in the maintenance plan (no plan for interval is documented). When the 5 % difference criteria is exceeded calibration is performed or at least every three months (the criteria not documented).

FEMMAN TEOM: PM10 Artig service	Intervall	Jan	Feb	Mars	April	Maj	Juni	Juli	AUG	Sep	Okt	Nov	Dec	Huvudansvar	Delansvar
		37811	1 817	mars	nyi ii	-		-20						ERIK S	HUNG
							dags								
TEOM-filter	<80% belastning														
Kylar-filter	Varje månad														
Bypass-filter	Var 6:e månad						vid service						dags!		
Partikelhuvud: byte/rengorning	Var 6.e månad						vid service						dagsi		
NOx: Teledyne		100000		1000000			THE PERSON NAMED IN	-			1000			HUNG	HELENE
Arlig service										dags				1000	
Sample-filter	Varje månad							-							
CO							-				THE RESERVE			HUNG	HELENE
Arlig service			- 1											HUNG	HELENE
Flaktfilter															
Sample-filter															
03	2000														
Arlig service						donal					2000			HUNG	HELENE
Sample-filter						dags									
302		-													
rlig service				donel										HUNG	HELENE
ample-filter				dags!											
asCal													1	1000	
lig service					7 10 10						77 13 15		1000	HUNG	HELENE
mikalibyte scrubbers				dags!											-
ancheck/kalibrering						7									
	ar 14:e dag				100		The contract				-		1	HUNG	
-	ar 14:e dag arje månad													nunu	HELEN
V.						12000									
2 (kalibrera endast span) Va	r 14:e dag	-	140000	1									-		
slangar (Va	irje månad														
			190 1												
	r 6:e månad			dags?											100000000000000000000000000000000000000
inläggning			2008		1000	60 1100				dags?					
service									Street, Square, Square,			13.130	Land I	HELENE	



- **b:** Are there written SOPs for maintenance, calibrations? There are some written instructions for maintenance and calibration at the station in Swedish/English, see photos in 5.d. Some of them are prints of the instrument manual. For ozone measurements, no instructions are documented since IVL takes care most of the instrument maintenance (but not all).
- **c:** Frequency of the maintenance of the analyser: The stations are visited at least every two weeks to perform the manual zero and span checks. Other maintenance is accomplished when needed. The data is visually checked three times a day at the office.
- **d: Actions during the maintenance:** Check for instrument operation and alarm lights, zero and span checks, filter changes for gas and PM monitors, TEOM check and leak test, change on PM inlets, change of consumables when needed.





# SO2- instrumentet (EC9850) på Femman Kalibrering Stäng av loggningen. Koppla in gasslangen i inlet på SO2- instrumentet. Kolla att det kommer gas ur T-slangen. Vänta i ea 15 minuter tills instrumentet stabiliserats och notera värdet. Tryck pil upp 6) Tryck select 7) Tryck pil ner (till span) 8) Tryck enter 9) Tryck select för att hoppa mellan siffrorna 10) Justera siffroma till refkonc med hjälp av pil upp eller pil ner. 11) Tryck enter Tryck enter Tryck pil ner till instrument gain. Tryck enter 13) Tryck enter 14) Tryck enter 15) Tryck exit (main menu) 16) Titta så instrumentet visar refkonc, om det inte, gör om från steg 5, tills det är ok. 17) Koppla ur slangen. 18) Stång av gasen. 19) Koppla in utomhusluftsslangen i instrumentet Sample gas inlet. 20) Sätt på loggningen. 21) Fyll i loggboken Kontroll av lampstyrka: кмацон av tampstyrкa: [astrument status (skriv ner värden) : High voltage: 708 V Lamp current 34,95 mA SO2 calibration, practical

3.1.1 Analyzer Calibration Instructions Note Note
This procedure is a quick guide to span calibration of the EC9850 analyzer, intended for operators who are familiar with gas analyzers and preparation of calibration gas. For complete gas preparation and multipoint calibration matructions please refer to section 3.2. Connect a source of span calibration gas to the analyzer through the Inlet port (see the remainder of this section for instructions on preparing calibration gas). Allow the analyzer to sample the gas until a stable reading is obtained, typically 15 minutes. From the primary screen start the calibration sequence by pressing either the Up or Down arrow (\* or \*) until the display prompts START MANUAL CALIBRATION. Pressing the "Select" key will allow you to choose from MO, SPAN or ZERO. Confirm that the display reads SPAN and press "Enter" (\_J). A backlit cursor will be displayed on the SO<sub>2</sub> concentration display. Use the <Select> key to move the position of the backlit cursor, and the Up
and Down arrow keys to increment and decrement the value of the backlit
digit until the calibration concentration value is displayed. When the desired
concentration is displayed, press <Enter>. Then move the backlit cursor to the INSTRUMENT GAIN field. The instrument gain is automatically calculated by the analyzer, Press <Enter> to confirm this value Press <Exit> to return to the primary screen. Note
The auto-zero function of the EC9850 eliminates the need for a traditional zero calibration. SO2 calibration, manual

## **TEOM 1405-DF**

## Byte av filter vid kylarna (2 st)

Byte en gång i månaden. Bara att byta, inga andra instruktioner krävs. Endast Thermo:s filter får användas!

## Byte av TEOM-filter

Görs innan 80% belastning.

Välj Service < Maintenance < replace TEOM filter. Följ instruktionerna på displayen.

#### Byte av bypass-filter

Bypass-filtren är de två mindre filtren på baksidan som sitter i horisontellt läge. De större filtren sor är i upprätt position är mot fukt. (De ska inte behöva bytas, men kolla dem då och då.)

Finns ingen instruktion för byte av bypass-filter, men eftersom det blir en uppstartsperiod efter filterbytet så välj Service < Maintenance < Replace TEOM filter på displayen. Byt filtren och gör läckagetest (se nedan).

Byt 2 ggr per år för PM10, mindre sällan för PM2,5 troligtvis – kolla hur smutsiga de ser ut.

Testet görs först och främst vid misstanke av läckage, men även efter byte av bypass-filter.

Det är bra om man är två när man gör detta eftersom en behöver vara uppe på taket.

Välj Service < Verification < Leak test

Följ instruktionerna på displayen (Ta bort TEOM-huvudet och sätt på avstängningsreglaget, stäng

OBS! Oklart om instrumentet ställer om till sommar/vintertid automatiskt



## e: Change of the particulate filter:

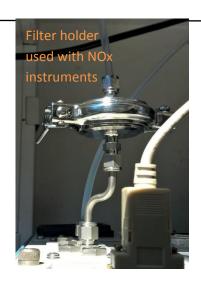
The internal filters are replaced once a month and the external filter for NOx every 3 months.

Filters are Millipore Teflon, pore size 5 µm.

The external filter is mounted in a stainless steel housing, see photo.

Filter housings are not cleaned.

<u>EN standards</u>: The filter housing shall be cleaned at least every six months.



**f: Zero and span checks: method and frequency:** With the calibrator at the site, performed manually every two weeks for NOx. No information about the frequency of other gases was available during the visit. Afterwards, information was shared: ozone is being checked four times a year (by IVL) and SO2 should be checked at least once a month but there has been some problems with the instrument lately so this has not been done so frequently.

EN standards: The zero and span checks should be performed at least every two weeks.

**g: Concentration of Span:** Span concentrations for analysers: 80 ppb for SO2, 400 ppb for NO and 40 ppb for O3.

Gas	Cylinder	Certificate	Nominal	Analyzed	Exp	Date of	Date of
standard		nr	(ppm)	(ppm)	uncertainty	analysis	expire
CO in N2	N15RKED	9480029001	2000	1999	1 %	3.11.2016	3.11.2019
NO in N2			50	50.5	2 %		
SO2 in N2			22	21.63	2 %		

h: Action criteria for zero and span: According to EN standards for span:  $\geq 5.0$  % of initial span value. For NOx and SO2 zeros, 1-2 ppb is considered the limit value (not documented) and this is within the EN standard criteria ( $\leq$  -4 or  $\geq$  4 nmol/mol).

**i: Check of field (span) standard:** The standards are not checked by a calibration laboratory since such a laboratory does not exist in Sweden. The gas standard is considered valid for one year after purchase. The gases are checked against the analyzers at Femman every six months.

<u>EN standards:</u> The stability of the gases used for span and zero checks shall be verified at least every six months with use of reference gases traceable to (inter)nationally accepted standards. These gases shall fulfil the specifications in Table 1.

**j: Frequency of the calibration:** Every three months for NOx and SO2 and every six months for O3, or after exceedance of span and zero criteria. Calibration is conducted with the same system as span checks (two-point calibration).

EN standards: Calibration shall be performed at least every three months for all gases.

The timings of last calibrations were reviewed at Femman. For NOx, this was accomplished with two previous calibrations occurring in 17.11.2016 and 11.1.2017. For SO2, this has not been



accomplished according to the station log book with last calibrations performed in 28.7.2016 and 27.10.2016. However, the missing calibration is less than one month delayed at this point. For O3, the last calibrations were conducted in 15.8.2016 and 16.11.2016 by IVL and thus the next calibration was due on the next day following the audit according to the interval described in EN 14625.







**k:** Check of linearity: Once a year for NOx, last done in 17.3.2016. Once a year for ozone, no date available for the last check. No information of SO2 provided. Documentation was not assessed.



I: Check of converter efficiency (NO-NOx analyser): Once a year by the manufacturer, last done in 22.11.2016. Documentation was not assessed.

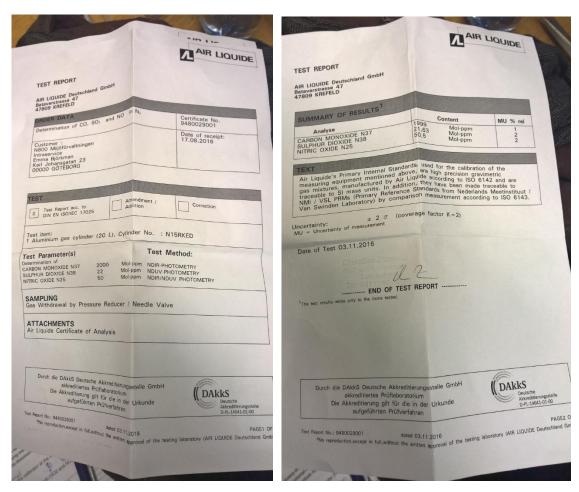
## m: Traceability of calibration standards (ISO 17025; 5.6) :

The traceability of the gas mixture standard at Femman is to NMi VSL (the Netherlands) Primary Reference Standards, see photo below for the certificate.

The gas standard at Femman is of higher quality than the gas standards at other stations. The gas standards at other stations are calibrated every six months with the analyzers at Femman and thus the traceability at other stations is through the gas standard at Femman.

The ozone calibrator maintained by IVL is traceable via University of Stockholm, Department of Applied Environmental Science (ITM), likely to NIST USA SRP (information not available).

The national reference laboratory does not organize intercomparisons, and thus the network does not participate in any intercomparisons regarding gas measurements.



- **n:** Where does the traceability of the calibration standards lead: As described above.
- o: How often the field calibration equipment/facility is calibrated against the reference standard (e.g. in the calibration laboratory): Span gas cylinder at Femman is not calibrated but used for a maximum of one year. The gas standards at other stations are calibrated against the gas standard at Femman twice a year. The operation of calibration equipment is checked by the manufacturer once a year during the annual maintenance.



## p: Estimation of the expanded uncertainty of the field measurements (5.4.6):

The uncertainties are calculated annually only for NOx since the other instruments are not type approved and hence do not have appropriate excel sheets. The measurement uncertainty is 8.5-11.6 % depending on the instrument. This uncertainty is annually reported to Swedish EPA.

## 6. Zero gas

a: Means of preparation of zero gas at the station:

Ambient air with three-stage external scrubbers, see photo in 5.j.

**b:** How often the scrubbing materials are changed inside the zero air generator: Once a year, last done in July 2016.

## 7. PM measurements

- **a: QA/QC procedures conducted for the measurements, see in Table 2.** At the site, there is printed instructions for PM measurements that includes leak test and change of different filters (see photo in 5.d). The operations are documented in station logbook. In addition, the following procedures:
  - The operational parameters are manually checked three times a day at the office.
  - Calibration of sensors for temperatures, pressure and humidity is performed once a year
  - No checks of the sensors are performed. The network does not use CEN/TS 16450:2013 or FprEN 16450.

<u>FprEN 16450 standard</u>: Where temperature, pressure (difference) and/or relative humidity sensors are essential to assure the accuracy of the PM mass concentration measurement made by the instrument, these shall be checked using appropriate transfer standards with readings traceable to (inter)nationally accepted standards. These checks shall be performed before the flow rate check. Minimum frequency every three months, please, see NOTE 8.4.4.

Calibration and checks of the AMS flow rates are done once a year, last in 30.8.2016.

<u>FprEN 16450 standard</u>: Checks of instantaneous flow rates shall be performed using an appropriate flow meter with readings traceable to (inter)nationally accepted standards. Minimum frequency every three months.

- Leak check of the sampling system is performed every six months.
- Some checks and regular maintenance of components of the AMS measuring system are performed when needed.

## b: How often the sampling inlet is cleaned and how?

See photo of the inlets at both stations below. The inlet at Gårda is secured against any interferences with a metal cage. At Femman, the inlet is cleaned twice a year and at Gårda and



other street stations four times a year. The cleaning is done by wiping the surfaces with a paper towel wetted with deionized water.





**c:** Do you crease the impactor plate of the inlet: Since the network is using US-EPA inlets, greasing is not needed.

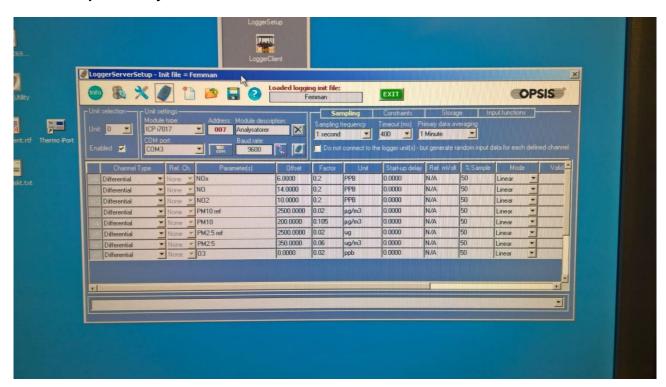
## d: Demonstration of equivalence with the reference method:

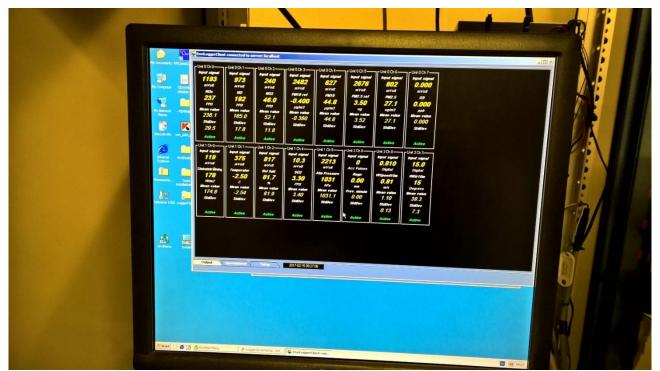
In 2013, an intercomparison between Gothenburg, Malmö and Stockholm was organized. A set of TEOM instruments were compared with the gravimetric reference method maintained by the Stockholm University. The results can be found in <a href="http://www.aces.su.se/reflab/wp-content/uploads/2016/11/ACES">http://www.aces.su.se/reflab/wp-content/uploads/2016/11/ACES</a> Report 4.pdf.

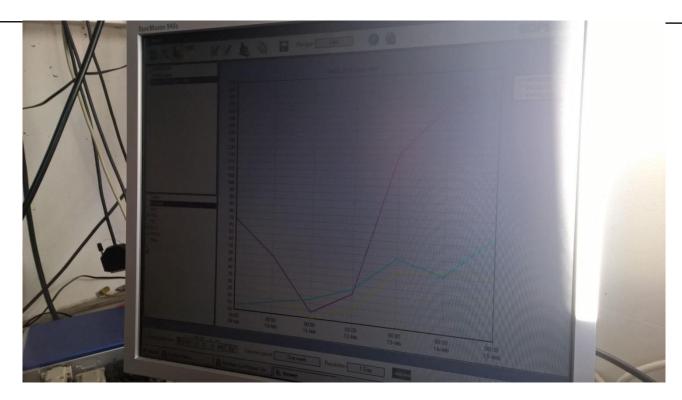


## 8. Data collection

a: Data acquisition system: EnviMan







**b:** How the data is sent to central data collection server: Every minute by GPS router.

#### c: Data validation routine?

Data validation is done once a month. There are no written instructions for the task since only one person is performing it. No automatic checks or flags are applied on the data. Manual checks are performed by all the four responsible persons without a set criteria, instead it relies on the expertise of the small group. Data validation is performed in excel sheets, which are later downloaded to the web page for public access. An annual final verification of the data is performed. Finally, the data is annually reported to Swedish EPA and published in the city's own reports.

## e: Is there any QA/QC procedures for data validation and reporting?

There are no SOPs for validation or reporting. EPA provides annually an excel sheet, which is then filled in accordingly.

### 9. Documentation

## a: Are there logbooks for the measurements and maintenance at the station?

The logbook is maintained in manual written form stored at the site, please, see photo below. The information is then transformed into electronic format at the office after station visits. Monthly checks are performed to make sure all the markings in the station log book are copied electronically.



Datum	1	Tid in	Tid ut	T200	TECAN (C): Ser-	PM10	SO2 O:	co	Anteckningar (fel, åtgärd mm) Utfört av
29	1/8	10:00					X		Noth-orn spanchock innon
									inst. h'(1 service Fick aubryta efferson instrumentel vour i stor up-ruccle stromaubrott? Nicht - o spart che de L
29	18	10:50	11:30	X					filtenbyte x 2 Em
30,	8	11:00				X			skowsh
16	19	7:10		X					Noll-o spancheck E
5/	10	10:25	10140					X	Nothing =
51	110	10:40	11:25	X					Noll-o spanchek Tomb E
19/1	0	11:20	12:20	X					Noll-c spanchock TECAN I
	10	8150	9:40	X					502 hilbaka fran seurto E. Logguing au TECAN B
		3:10			X	1	X		Logguing au TECAN B
3/11		7:30	8:10		X	1			Noll-o spanchock to
3/1		9:10	9:15	X	1				_11 _ 11

b: Does anyone check the log books? Checked monthly, see 9.a.

c: Where do the manuals of the equipment locate?

Most of the manuals are located at the sites and rest of them in the office. Manuals are in English.

## 10. Audits

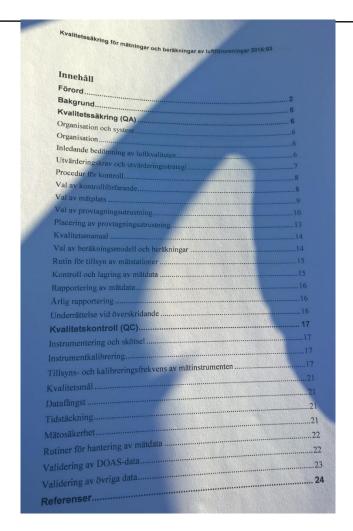
## a: Have there been any external audits and if by whom?

Not officially. The UK reference laboratory NPL made an interview and visit to station in 2014 but no report was prepared.

## 11. Quality System (QS), Reference to ISO 17025

The network has a "light version" of quality system with some documentation like instructions, logbooks and calendars but the network has no Quality Manual and does not utilize EN ISO/IEC 17025. Annually, a report titled *Quality assurance for measurements and calculations of air pollution* is published (see photo below for contents).





**a:** Does the QS include the station activities? If so reference to SOP. There are no official SOPs but some instructions described in 5.d.

## b: How is the QS implemented at the station?

There are several instructions that include activities performed at the station. The maintenance calendar is documented at the station (shown in 5.a).

#### c: Are the relevant SOPs available at the station?

Yes, the most relevant instructions are available in paper prints at the site. The list of instructions is given below:

- Instructions for zero and span checks and calibration of all the instruments.
- Instructions for changing the filters on the TEOM.
- Instructions for cleaning the TEOM inlet.
- Instructions of how use the GasCal.

#### d: Check and comments of the SOPs relevant to AQ measurements at the site.

Most of the instructions are in Swedish. The instructions are not covering all the activities at the site.



<u>e:</u> Complains (4.8) There is no register for complaints. Sometimes complains have been received from EPA but mostly just questions.

<u>f:</u> Improvements (4.9) Not applicable.

g: Corrective actions (4.9) Not clearly documented, some in logbook.

<u>h:</u> Internal audits (4.14) Not arranged at the moment. It was discussed that when the new EN 16450 is published later this spring it might be really useful for the network to make an internal audit about PM measurements and assess if the EN 16450 is followed already or if some improvements are needed.

<u>i:</u> Personnel (5.2) The training of the personnel is not documented but includes about two months of training prior to working unaccompanied.

## **List of SOPs:**

No official SOPs available (see 11.c).

## **Comments and recommendations (summary):**

The network has a long experience of making air quality measurements. The technical level of the network is good but documentation could be improved. Some remarks about following the EN standards are given in the report *in italic* concerning nonconformities of QA/QC procedures for gases and PM. The network has no official quality system.

The technical specification CEN/TS 16450 for PM10 and PM2.5 measurements will be replaced by a new standard EN 16450 this spring (likely in April). The network should be acquainted with the new standard.

Report submitted:

Katriina Kyllönen, 20.3.2017



Table 1. The checks and calibrations together with their frequency; gas measurements

Calibration, checks and maintenance	Frequency	Action criteria			
Calibration of the analyser	At least every three months and after repair				
Certification of test gases	At least every six months	Zero: ≥ detection limit  Span: ≥ 5,0 % from last certified value			
Zero and span check	At least every two weeks	Zero: ≤ -4 or ≥ 4 nmol/mol (CO: -0.5 or 0.5 μmol/mol) Span: ≥ 5,0 % of initial span value			
Repeatability at zero and span of the analyser	In combination with calibration, using the data from the calibration	Repeatability standard deviation at zero: 1.0 nmol/mol (NO), 5.0 nmol/mol (SO2), 1.5nmol/mol (O3), 0.5 µmol/mol (CO)  Repeatability standard deviation at span: 0.75% (NO), 1.5 % (SO2), 2% (O3), 3% (CO)			
Lack of fit check (to be performed in laboratory or in field)	Within 1 year after installation and after repair; further frequency depending on the result of test	lack of fit > 4,0 % of the measured value lack of fit > 5 nmol/mol at zero (CO: 0.5 μmol/mol)			
Converter efficiency (NO)	At least every year	≤ 95 %			
Testing sample manifold -influence of pressure drop induced by the manifold pump - sample collection efficiency	At least every three years	influence > 1 % of measured value (pressure drop; 9.6.3/4.1)			



		influence > 2 % of the measured value (sample collection efficiency; 9.6.3/4.2)
Change of particulate filters c of the sampling system at the sampling inlet and/or at the analyser inlet	Depending on the results of a test as prescribed in 9.3, but at least every three months	Response to span gas passing the filter is ≤ 97 %
Test of the sampling lines	At least every six months	≥ 2 % sample loss
Changing of (if applicable): drying material and other consumables	At least every six months	As required
Regular maintenance of components of the analyser	As required by manufacturer	As required

a Span value: recommended concentration of 70 % to 80 % of the certification range for NO2 or 70 % to 80 % of the certification range of NO, depending on which check gas is used.

- b Recommended every 23 h or 25 h.
- c The particulate filter shall be changed periodically depending on the dust loading at the sampling site. During this filter change the filter housing shall be cleaned. Overloading of the particulate filter may change the concentration of nitrogen monoxide and/or nitrogen dioxide.
- d Dependent on site-specific conditions.
- e If infringement of an action criterion occurs, corrective actions shall be taken as soon as possible. An evaluation of the influence of the detected infringement on the measurement data produced before the actual correction of the infringement took place shall be given and taken into account during data validation. To ensure that the data capture criterion is met, data will need to be inspected by a trained operator every working day.
- f This requirement differs from the requirement in the type approval laboratory test. In this laboratory test the converter is new and therefore the requirement is more stringent and set at ≥ 98 %.

Table 2. QA/QC procedures for the automated PM analyzers

Calibration, checks and maintenance	Clause	Minimum Frequency <sup>a</sup>	Lab/ field	Action criteria <sup>b</sup>	Uncertainty requirements for transfer standards
Checks of status values of operational parameters (see 7.5.4)	8.4.3	Daily (on working days)	L/F	See below	
Checks of sensors for temperatures, pressure and/or humidity <sup>c</sup>	8.4.4	Every 3 months	F	± 2 °C ± 1 kPa ± 5 % RH	
Calibration of sensors for temperatures, pressure and/or humidity <sup>c</sup>	8.4.5	Every year	L/F		1,5 °C 0,5 kPa 3 % RH
Check of the AMS flow rate(s)	8.4.6	Every 3 months	F	± 5 %	2 %
Calibration of the AMS flow rate(s)	8.4.7	Every year	L/F		1 %
Leak check of the sampling system	8.4.8	Every year	F	± 2 %	
Zero check of the AMS reading	8.4.9	Every year	L/F	± 3 μg/m³	
Check of the AMS mass measuring system	8.4.10	As recommended by the manufacturer and after repair, but at least every year	L/F	as set out by manufacturer, or ± 3% if necessary	
Regular maintenance of components of the AMS	8.5	As required by the manufacturer	L/F	as set out by manufacturer	

<sup>&</sup>lt;sup>a</sup> Frequencies of checks and calibrations may be relaxed when sufficient history exists demonstrating that drifts of sensor readings and flow rates remain within the specified requirements.

b With reference to nominal values.

<sup>&</sup>lt;sup>c</sup> For some instruments such checks and calibrations are not possible in situ because of the positioning of the sensors within the AMS. Therefore, these checks and calibrations are restricted to sensors that are accessible in the field (typically in the sampling head). As a part of the annual checks, the checks may be performed in a laboratory room with constant temperature and relative humidity by comparing sensor readings (after stabilization) with those of reference standards.



## **SYSTEM AUDIT REPORT**

## Auditors:

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## **SYSTEM AUDIT REPORT**

(P) Measurement station: Mineral 24 Vasilivsky Island (VI)

(P) Location: (VI) Spedny Prospect, 74

Raporteur: Kaisa Lusa, Jari Walden

Representatives: Vasily Litvinenko, Alexander Chukov, Dimitry Koltsov

**Date of audit:** 5.6.2018

## 1. Measurement station

a: Site classification: Urban traffic station.

Purpose of the measurements: The station is part of the air controlling system in St. Petersburg City area. The measurement of gases (NO-NO<sub>2</sub>-NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>3</sub>) have been accredited according to EN ISO/IEC 17025:2005 since 2006.

Measurement components:

- NO-NO<sub>2</sub>-NO<sub>x</sub>, SO<sub>2</sub>, CO, O<sub>3</sub>, PM<sub>10</sub> & PM<sub>2.5</sub>
- No meteorological instrumentation

Measurement activities started: January 2017

## b: Description of the station:

The station is located on Vasilivsky island on the side of Geological Institute and surrounded by buildings. The site is locked and very well guarded.

Photos around the station:





## c: Environmental conditions:

During the audit it was cloudy, rainy, windy and the temperature was 12°C.

## d: Overview of the station:

See the map and the photo below:





## 2. Personnel of the station

## Responsible person:

Alexander Chukov – Senior Engineer of State Company Mineral

Alexey Berestain – Engineer of State Company Mineral

Also other staff of laboratory

## 3. Sampling line

## Sampling manifold:

a: Material: Stainless steel with Teflon tube

b: Length of the manifold: About 40 cm

c: Flow rate inside the manifold: 4,5 l/min

d: Check of the sampling line: At least once in three months, if needed more often.

e: Testing of the manifold: At least once in three months and cleaning annually.

## 4. Analyzers:

## a: Analysers at the station:

- NO-NO<sub>x</sub>: Thermo 42C

- CO: CO 12M Environnement s.A

- O<sub>3</sub>: Horiba APOA-370

- PM<sub>2,5</sub>: Derenda

- Zero gas: Filtered air and zero air generator.

See photos below:





## b: Analysers in the laboratory:

- NO<sub>x</sub>: AC32M Environnement s.A
- SO<sub>2</sub>: AF22M Environnement s.A, Thermo 43C, Horiba APSA-370 (2 pcs)
- CO: CO 12M Environnement s.A (3 pcs), Thermo 48C (2 pcs)
- O<sub>3</sub>: O<sub>3</sub> 42M Environnement s.A

## See photos below:









## c: Calibrators in the laboratory:

- Thermo 146C Dynamic Gas Calibrator (3 pcs)
- APMC-370 Air Pollution Multigas Calibrator

## See photos below:





## d: Zero air in the laboratory:

Purified air is made by filtered air and by zero air generators. See the photos below:





## 5. Maintenance and calibrations

## a: Maintenance and calibration plan?

There are two levels of calibrations:

- All air quality analyzers in all stations in the St Petersburg network are checked annually by VNIIM.
- 2. The staff of State Company Mineral calibrates the analyzers at least once in 1 month.

If the criterions are not fulfilled the analyzer will be taken to the laboratory for the adjustment and maintenance.

## b: Are there written SOPs for maintenance, calibrations?

Yes there are, see annex 1 the list of the SOPs.

## c: Frequency of the maintenance of the analyser:

If the criterions are not fulfilled the analyzer will be taken to the laboratory for the adjustment and maintenance.

## d: Actions during the maintenance:

Maintenance actions are maintained according to the requirements of the Guidance of Continuous Air Quality Monitoring set by the Ministry of Natural Resources and Environment of Russian Federation (See the list of the SOPs, annex1).

e: Change of the particulate filter: At least once in 3 months

## f: Zero and span checks: method and frequency:

Zero check: once a week, performed automatically every weekend during nighttime using purified air made by a filter. Material of the filter is unknown because the product has been developed for



the purpose of Russian army. Material has been tested in the Laboratory of Mineral and it found to be usable for purifying the zero gas.

Span check: once in 2 weeks - 1 month (min 1 month). Three gases gas mixture is prepared in the laboratory by diluting VNIIM certified gas standard (mixture of CO, NO, SO<sub>2</sub>). Prepared calibration gas is stored in plastic bags. Four plastic bags have been connected together for having larger volume for the calibration gas. Calibration gas mixture will be used within one hour for the purpose of avoiding changes in concentration levels. The idea of using these plastic bags is that when measuring the calibration gas the concentration levels of the analyzers will stabilize rather quickly. The system is light to carry and also easy to use so it decreases possibilities for mistakes at the station. See photos below:





## g: Concentration of Span:

NO: about 200-350 μg/m³
 SO<sub>2</sub>: about 180-250 μg/m³
 CO: about 1,0 – 1,5 mg/m³

## h: Action criteria for zero and span:

Zero and span checks are maintained according to the requirements of the Guidance of Continuous Air Quality Monitoring set by the Ministry of Natural Resources and Environment of Russian Federation.

### i: Check of field (span) standard:

Calibration gas mixture is prepared in the laboratory.

## j: Frequency of the calibration:

All analyzers are calibrated annually by VNIIM and the staff of Mineral calibrates the analyzers at least once in 1 month.

### k: Check of linearity:



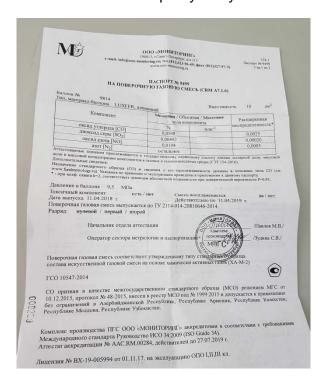
Linearity is checked annually and also if there has been made some maintenance for the analyzer.

## I: Check of converter efficiency (NO-NOx analyser):

Once a year.

## m: Traceability of calibration standards (ISO 17025; 5.6) :

The traceability of the gas mixture standard at Mineral is to VNIIM primary reference standard, see below the photo of the certificate. Also flows of the gas calibrators are traceable to VNIIM. In addition to this all air quality analyzers in all stations are calibrated annually by VNIIM.



## n: How often the field calibration equipment/facility is calibrated against the reference standard (e.g. in the calibration laboratory):

Field calibrations are made using VNIIM certified reference standards.

## o: Estimation of the expanded uncertainty of the field measurements (5.4.6):

Estimation of uncertainty is going on. Uncertainty estimation is about 10-15% and the requirement for the uncertainty is ±25% according to the Guidance of Continuous Air Quality Monitoring set by the Ministry of Natural Resources and Environment of Russian Federation.

### 6. Zero gas

## a: Means of preparation of zero gas at the station:

- 1. Zero air filter
- 2. Perma Pure zero air generator

### b: How often the scrubbing materials are changed inside the zero air generator:



Once a year.

#### 7. PM measurements

The data is collected into the database at the site (micro-pc) and also the on-line data is collected into the data server at the office. In case of PM analyzers the concentrations of 20 min averages are collected and stored in the database. Other parameters from the PM-analyzers are e.g. flow rate but it is not stored in the database.

- a: QA/QC procedures conducted for the measurements, see in Table 2. The instruction for checks of operation of automated PM analyzer, PNS16D-APM for PM10/PM2.5 by Comde Derenda, Germany (<a href="www.comde-derenda.com">www.comde-derenda.com</a>) instruments have been prepared and stored at the office. The technician being responsible for the method brings the instruction and the measurement logbook to the site where the checks are reported. Such checks includes:
  - Check of the operation of the analyzer
  - Check of flow rate
  - Temperature

Calibration of the sensors for flow rate, temperature, and pressure:

- Once a year, VNIIM calibrates the flow sensor and the nephelometer

Leak check of the sampling line

every 4000 working hours (=> approx. twice a year if continuous sampling)

## Zero check

- There is an automatic check of the zero line by the nephelometer

## Sampling line:

Reference sampler

- The size selective inlet for filter sampling is cleaned and creased every 3 months
- The inlet type is EU (contructed according to EN 12341 by Comde Derenda).

Nephelometer

- No size selective inlet (optical method) either by pass flow (1:200) at isokinetic condition or by separate inlet (flow rate 0,2 l/min).

The operation of the nephelometer is checked once a month with the reference sampler by using the glass fibre filter in parallel measurement with the nephelometer at time intervals of 24 h to one week. Correction factors are within the ranges from 0.5 to 1.8. Such a lage variation is an indication of the different sources of particles, different meteorological conditions (winter/summer; dry/wet)

d: Demonstration of equivalence with the reference method:



The equivalence of the PNS16D-APM is not conducted for the specific model. The sampler parts fulfills the requirements for the reference sampler according to EN12341:2014. The size selective inlet is also tested by TYV. The next generation of APM-2 i.e. the automated PM analyzer using the nephelometer technique has also proven to be equivalence by TYV (Certificate number 40336/2014, valid until 2019).

## Weighing system for the reference method

The weighing of the filters sampled with the PNS16D-APM is conducted with an automated weighing system by Combe Derenda.

## Operating principle and weighing process

Before weighing takes place, the system settings and all the parameters for the forthcoming weighing job are entered in the PC using the *AWS Control* software. Next, the unladen sampling filters are placed in the filter disc magazine of the AWS-1 by hand. The filters are then preconditioned in the closed weighing chamber for a user-specified period of time, e.g. according to EN 12341 for 48 hours, at preselected temperature and humidity. If the filters are to be identifiable, their edges are punched with a code by the optional coding station.

The next step is the first weighing series, which consists of weighing the unladen filters, usually in two weighing passes. All the selected filters are thus consecutively weighed once and then for a second time. If discrepancies lying outside the specified tolerances are recorded between the first and second weighing passes, the relevant filters are weighed again in a third pass. The carrier fork automatically transports the filters between the system components (e.g. magazine  $\rightarrow$  coding station  $\rightarrow$  balance  $\rightarrow$  magazine). The optional ionization fan neutralizes the filters ("eliminates" the static electricity) and thus enhances weighing accuracy.

Once the unladen filters have been weighed, they are placed in filter cartridges and installed in a dust sampler or other sampling system. Sampling then takes place according to EN 12341 – as a general rule, each filter is exposed to airborne dust for 24 hours.

After sampling, the filters are returned to the filter disc magazine and conditioned again. The second weighing series (weighing the laden filters) follows, once again with two or possibly three weighing passes. Previously coded filters are identified by the reading station, which allows the laden reading to be compared directly with the preceding unladen reading. Both before and during the weighing series, verification weighing operations are performed with reference filters in order to monitor the climatic conditions inside the weighing chamber. During the weighing operation, all the data (weight values, mean values, weight difference between unladen and laden filters, and ancillary data, such as temperature and relative humidity) are saved in the database on the system PC.

The saved data can subsequently be exported for analysis and processing. The concentration of suspended particulate matter is calculated from the weight difference between the laden and unladen filters, giving consideration to the air flow rate during the collection period.

Table 2. QA/QC procedures for the automated PM analyzers

Calibration, checks and maintenance	Clause	Minimum Frequency <sup>a</sup>	Lab/ field	Action criteria <sup>b</sup>	Uncertainty requirements for transfer standards
Checks of status values of operational parameters (see 7.5.4)	8.4.3	Daily (on working days)	L/F	See below	
Checks of sensors for temperatures, pressure and/or humidity <sup>c</sup>	8.4.4	Every 3 months	F	± 2 °C ± 1 kPa ± 5 % RH	
Calibration of sensors for temperatures, pressure and/or humidity <sup>c</sup>	or sensors for strip year				1,5 °C 0,5 kPa 3 % RH
Check of the AMS flow rate(s)	8.4.6	Every 3 months	F	± 5 %	2 %
Calibration of the AMS flow rate(s)	8.4.7	Every year	L/F		1 %
Leak check of the sampling system	8.4.8	Every year	F	± 2 %	
Zero check of the AMS reading	8.4.9	Every year	L/F	± 3 μg/m³	
Check of the AMS mass measuring system	8.4.10	As recommended by the manufacturer and after repair, but at least every year	L/F	as set out by manufacturer, or ± 3% if necessary	
Regular maintenance of components of the AMS	8.5	As required by the manufacturer	L/F	as set out by manufacturer	

<sup>&</sup>lt;sup>a</sup> Frequencies of checks and calibrations may be relaxed when sufficient history exists demonstrating that drifts of sensor readings and flow rates remain within the specified requirements.

b With reference to nominal values.

<sup>&</sup>lt;sup>c</sup> For some instruments such checks and calibrations are not possible in situ because of the positioning of the sensors within the AMS. Therefore, these checks and calibrations are restricted to sensors that are accessible in the field (typically in the sampling head). As a part of the annual checks, the checks may be performed in a laboratory room with constant temperature and relative humidity by comparing sensor readings (after stabilization) with those of reference standards.



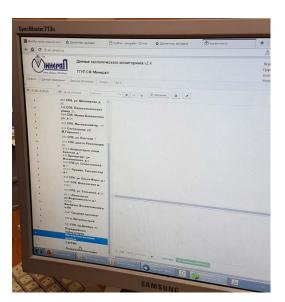
## 8. Data collection

## a: Data acquisition system:

At the present time data acquisition system is Airviro, but the new system (created in Russia) will be taken to use. The new system is already in testing.

See photos below.





### b: How the data is sent to central data collection server:

The data is collected into the data server at the office by modem.

## c: Data validation routine? Is there any QA/QC procedures for data validation and reporting?

Automatic checks are performed on the data by the Airviro software. It has an automatic datafilter, which removes the incorrect data. Other corrections are not being done.

All reports can be made by the Airviro software automatically and also in future by the new Russian version.

Because the new software is still in testing it is possible to make development to the new system.

## 9. Documentation

## a: Is the logbooks for the measurements and maintenance at the station?

The logbooks are maintained as written form including following details:

- date



- action
- person
- service
- calibrations
- daily works of the system

## b: Does anyone check the log books?

Accreditation companies.

## c: Where do the manuals of the equipment locate?

In the laboratory.

## 10. Audits

## a: Have there been any external audits and if by whom?

- Once in two years: Federal Accreditation Service
- Once a year: Committee for Use of Natural Resources, Environment Protection and Environmental Safety of Saint Petersburg City Administration

## 11. Quality System (QS), Reference to ISO 17025

## a: Does the QS include the station activities? If so reference to SOP

Yes, the measurements at the station are accredited and described in SOPs (see annex1).

## b: How is the QS implemented at the station?

The measurements of the gases are accredited. There are several SOPs that include activities performed.

An external checking is performed at the station every year by VNIIM.

See the photo of the accreditation certificate below:





#### c: Are the relevant SOPs available at the station?

All the SOPs are stored in electronic format. See the list of the SOPs in annex1.

### d: Check and comments of the SOPs relevant to AQ measurements at the site

## e: Complains (4.8)

Not needed (no customer works).

## f:\_Improvements (4.9).

Improvements are made e.g. according to suggestions of internal audits and accreditation assessments.

## g:\_Corrective actions (4.9)

Treatment of corrective actions is stated in the SOP (list of the SOPs in annex1).

## h:\_Internal audits (4.14)

Internal audits are performed.

## i:\_Personnel (5.2)

Procedures of the training of the personnel:

- Annually special 5-10 days course organized alternately in various cities (e.g. Moscow, St Petersburg)
- Training of manufacturers (e.g. Derenda)

### j: List of SOPs:

See the annex1.

## **Comments:**

The network has a long experience of making air quality measurements. Quality System of the measurements is based on the requirements of the Guidance of Continuous Air Quality Monitoring set by the Ministry of Natural Resources and Environment of Russian Federation. The measurements of gases are accredited according to EN ISO/IEC 17025:2005 and assessed every two year by the official accreditation body and annually by the Committee for Use of Natural Resources, Environment Protection and Environmental Safety of Saint Petersburg City Administration.

#### Annex 1

- Регламент обслуживания Автоматизированной системы мониторинга атмосферного воздуха Санкт-Петербурга, 2013 г.
- 2. Станция контроля загрязнения атмосферного воздуха автоматическая унифицированная УС-КВ-1, 2016 г.
- 3. Автоматическое устройство градуировки газоанализаторов, калибратор для поверки газоанализаторов модель 146С Thermo Electron. Инструкция по эксплуатации.
- 4. Газоанализатор озона модель 49С Thermo Electron. Инструкция по эксплуатации.
- 5. Газоанализатор диоксида серы модель 43C Thermo Electron. Инструкция по эксплуатации.
- 6. Газоанализатор оксидов азота и диоксида азота модель 42C Thermo Electron. Инструкция по эксплуатации.
- 7. Газоанализатор оксида углерода модель 48C Thermo Electron. Инструкция по эксплуатации.
- 8. Генератор нулевого воздуха ГНГ-01. Инструкция по эксплуатации.
- 9. Генератор газовых смесей модель ГГС-03-03. Инструкция по эксплуатации.
- 10. Генератор термодиффузионный ТДГ-01. Инструкция по эксплуатации.
- 11. Анализатор моноокиси углерода с коррелирующим газовым фильтром, СО12М. Техническое руководство.
- 12. Хемилюминесцентный анализатор окиси азота, модуль АС32М. Техническое руководство.
- 13. УФ фотометрический анализатор озона, модуль ОЗ42М. Техническое руководство.
- 14. УФ флуоресцентный анализатор двуокиси серы, АF22М. Техническое руководство.
- 15. Генератор нулевого воздуха ZAG2007, Руководство по эксплуатации.
- 16. Устройство сбора взвешенных веществ PM10, PM2,5 на фильтр LVS3.1/PNS3.1-15, Comde Derenda. Руководство.
- 17. Газоанализатор содержания формальдегида (H2CO) Picarro G2107. Руководство пользователя.
- 18. Универсальный пробоотборный насос №224-РСХR8 SKC Inc.. Руководство пользователя.
- 19. Автоматический аспиратор для сорбционных трубок GSU, Comde Derenda. Руководство по эксплуатации.
- 20. Хроматограф газовый портативный, модель ФГХ-1, Экан. Руководство по эксплуатации.
- Хроматограф газовый Syntech Spectras GC955 модели 600. Руководство по эксплуатации.
- 22. Система взвешивающая автоматическая тип AWS-1. Руководство по эксплуатации.



- 1. Станция мониторинга атмосферного воздуха
- 1.1. Стационарная станция
- 1.1.1. Порядок осуществления контроля работы станции
- 1.1.2. Установка/Снятие пробоотборных фильтров, пакетов и сорбционных трубок
- 1.2. Передвижная лаборатория
- 1.2.1. Порядок осуществления контроля работы передвижной лаборатории
- 1.2.2. Порядок выполнения измерений концентраций углеводородов с использованием хроматографов: ФГХ-1, Synspec GC955 601, Picarro G2107 на передвижной лаборатории.
- Порядок проведения контрольных измерений на станции мониторинга атмосферного воздуха
- 1.4. Поверка станции мониторинга атмосферного воздуха
- 2. Участок технического обслуживания, сбора, приема и передачи информации
- Участок технического обслуживания газоанализаторов и вспомогательного оборудования
- Порядок проведения диагностики, профилактических и ремонтных работ газоанализаторов и устройств системы автоматического пробоотбора взвешенных частиц
- Порядок проведения диагностики, профилактических и ремонтных работ поверочного оборудования
- 2.1.3. Регламентное обслуживание метеорологического оборудования
- 2.1.4. Регламентное обслуживание вспомогательного оборудования
- Технологический участок отбора проб на фильтры, сорбенты и анализа ЛОС
- Регламентное обслуживание и градуировка хроматографов GC 955 600 и GC 955 601
- 2.2.2. Регламентное обслуживание и градуировка ФГХ-1
- 2.2.3. Калибровка и регламентное обслуживание аспираторов GSU
- 2.2.4. Порядок проведения очистки пробоотборных пакетов
- 2.2.5. Порядок проведения очистки сорбционных трубок
- Порядок проведения измерений для определения ЛОС с использованием пробоотборных пакетов
- 2.2.7. Регламентное обслуживание системы AWS-1
- Порядок проведения взвешивания фильтров для определения массовой концентрации взвешенных веществ и корректировки поправочного коэффициента.
- 2.3. Участок сбора, приема и передачи информации



## Приложения:

- 1. Инструкция по калибровке каналов аспираторов GSU.
- 2. Инструкция по очистке пробоотборных пакетов.
- 3. Инструкция по очистке сорбционных трубок.
- 4. Инструкция по градуировке газовых хроматографов Synspec GC 955 600 и GC 955 601.
- Инструкция по анализу проб воздуха с использованием пробоотборных пакетов на газовом хроматографе Synspec GC 955 600.
- Инструкция по проведению процедуры взвешивания фильтров для определения массовой концентрации взвешенных веществ и корректировки поправочного коэффициента.
- 7. Инструкция по подключению драйверов при установке/замене газоанализаторов на станции.
- 8. Инструкция по проведению контрольных измерений.