Interreg
Baltic Sea Region
EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND
EnviSuM

EnviSuM

WP3 Air quality and deposition/Activity 3.3 Urban measurements

Urban Air Quality Measurements

Jari Waldén, Katriina Kyllönen, Mika Vestenius, Kaisa Lusa,
Jatta Salmi, Sisko Laurila, Jaakko Laakia, Karri Saarnio

Contents

1. Introduction 2

2. Measurement sites 3

2.1 Measurement site in Gdansk 3

2.2 Measurement site in Gothenburg 4

2.3 Measurement site in St. Petersburg 6

3. Comparison events and audits 7

3.1 Comparison of PM measurements against the reference method 7

3.2 PM instruments for the comparison 9

3.3 Calibration of the gaseous analyzers 14

3.4 Analysis of results 15

3.5 Quality management system audit 15

4. Results 17

4.1 PM comparison in Gdansk 17

4.2 PM comparison in Gothenburg 22

4.3 PM comparison in St. Petersburg 27

4.4 Gaseous air pollution from Gdansk, Gothenburg and St. Petersburg 31

4.5 Summary of comparison and calibration results in Gdansk, Gothenburg and St. Petersburg 33

4.6 System audits from pilot cities 34

Summary 36

References 39

Annex 1. Protocol for conducting the comparison studies in EnviSuM project 41

Annex 2. Equivalent test results 46

Annex 3. System audit reports 52

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_x, SO_x, CO, O_3, PM_{10}, and $PM_{2.5}$.

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_{10} and $PM_{2.5}$ 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_x, SO_x, CO and O_3,
- reference samplers for side-by-side comparisons of PM_{10} and $PM_{2.5}$ 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_{10} and $PM_{2.5}$ 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 (https://armaag.gda.pl/en/index.htm) 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 air quality network (Figure 2.2a) is operated by the City of Gothenburg (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_{10} comparison was conducted at station No. 4 whereas $PM_{2.5}$ 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_{10} comparison took place at station No. 4 and at station No. 10 $PM_{2.5}$ 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 ± 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^3/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^3. 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 $a = 3$ µg/m^3, $b = 1.03$ and C is the measurement signal. The factory settings were used at ARMAAG network (AM8 for $PM_{2.5}$ 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 β-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_{10} 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 β-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_{10} and $PM_{2.5}$ at a sample flow of 1 m^3/h. The sample inlet was one of the commercial types designed according to the EN-standards for $PM_{2.5}$ and PM_{10}. The measurement range for normal operation is from 0 µg/m^3 to 5000 µg/m^3.

Figure 3.3. *FH 62-I-R*

IVL PM_{10} sampler

The IVL PM_{10} 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_{10} 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_{10} 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_{10} 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_{10} 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 µg/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_1, $PM_{2.5}$ and PM_{10}. 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 (http://ec.europa.eu/environment/air/quality/legislation/assessment.htm,). 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.

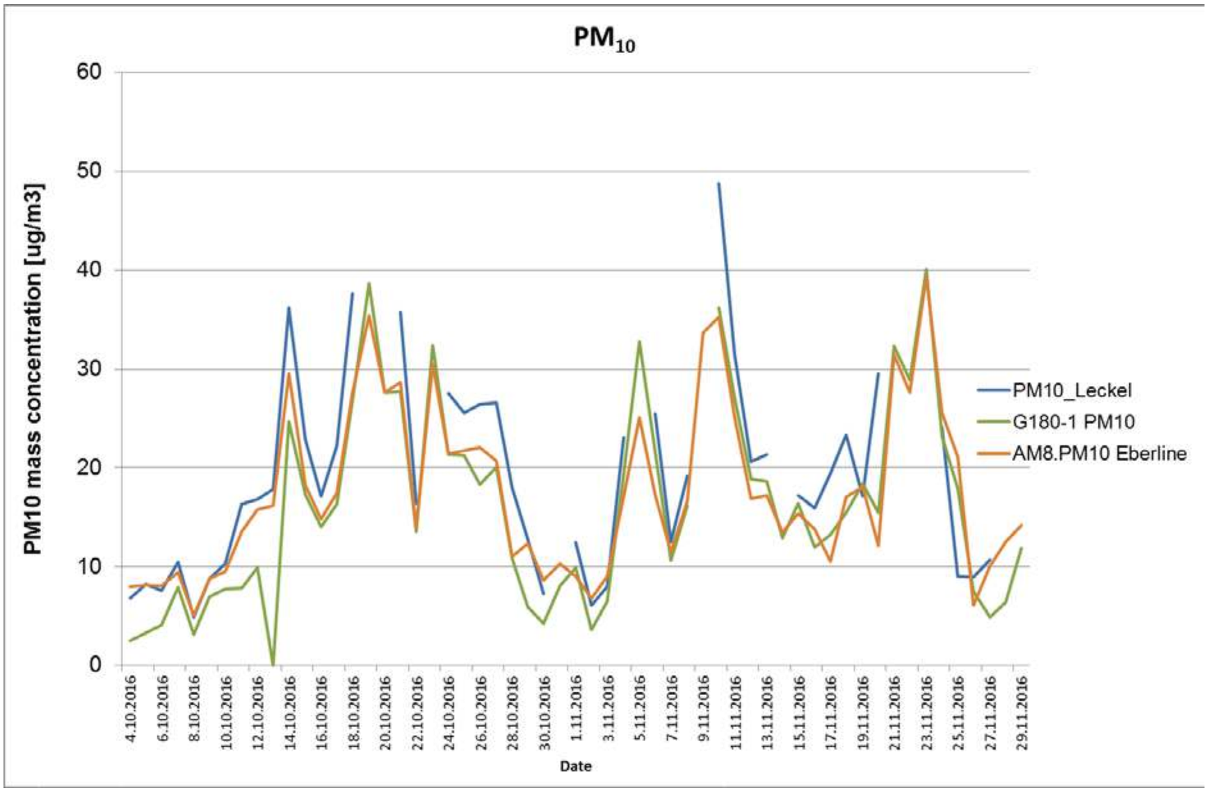


Figure 4.1. *The daily average values of PM_{10} mass concentration for site analyzer Eberline, optical analyzer by Grimm, and the reference method at station AM8 in Gdansk.*

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.

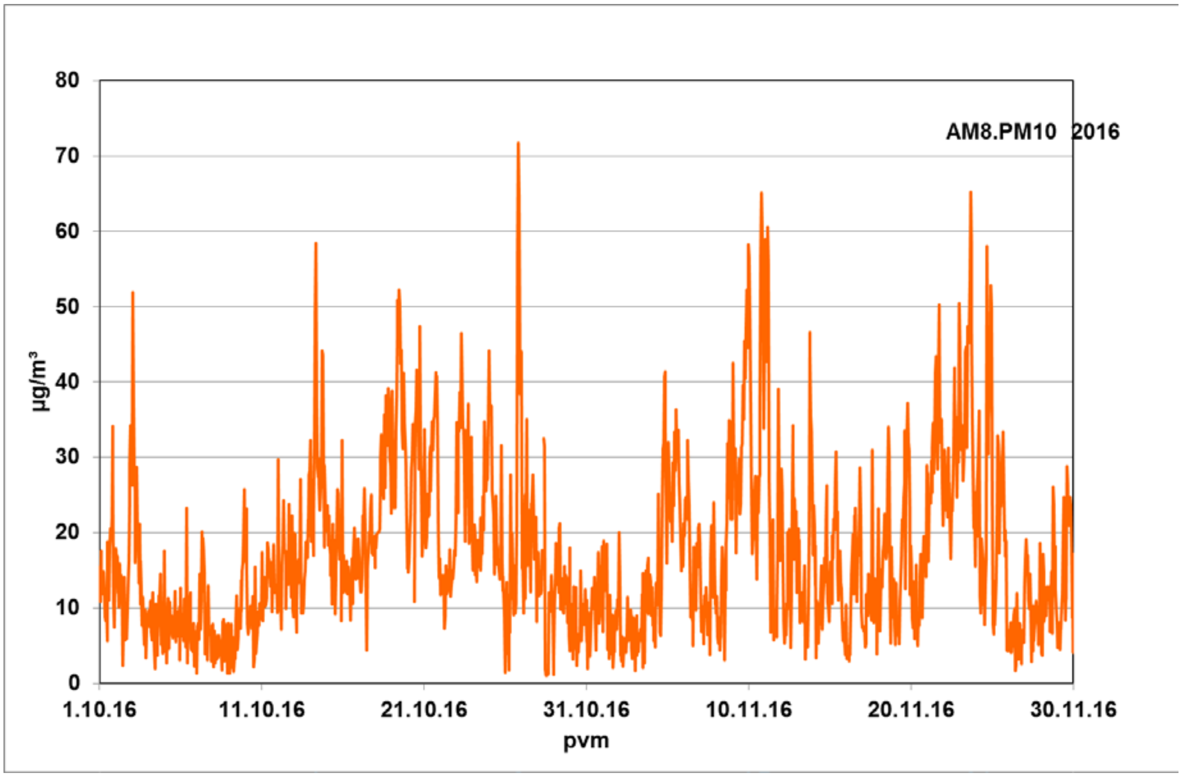


Figure 4.2. *Hourly averages for PM$_{10}$ mass concentration measured by site analyzer Eberline FH 62-I at AM8, Gdansk.*

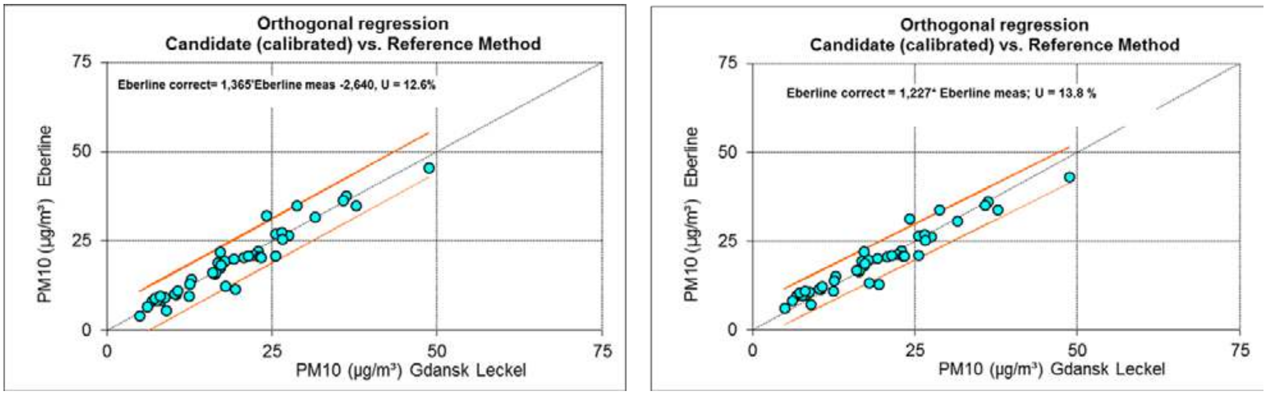


Figure 4.3. *Orthogonal regression analysis between the site analyzer for PM$_{10}$ at AM8 and the reference method. In the left, the calibration equation of type y = ax + b, where y is the corrected value of Eberline FH 62-I, a is the slope of the calibration equation, x is the raw value of Eberline 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.

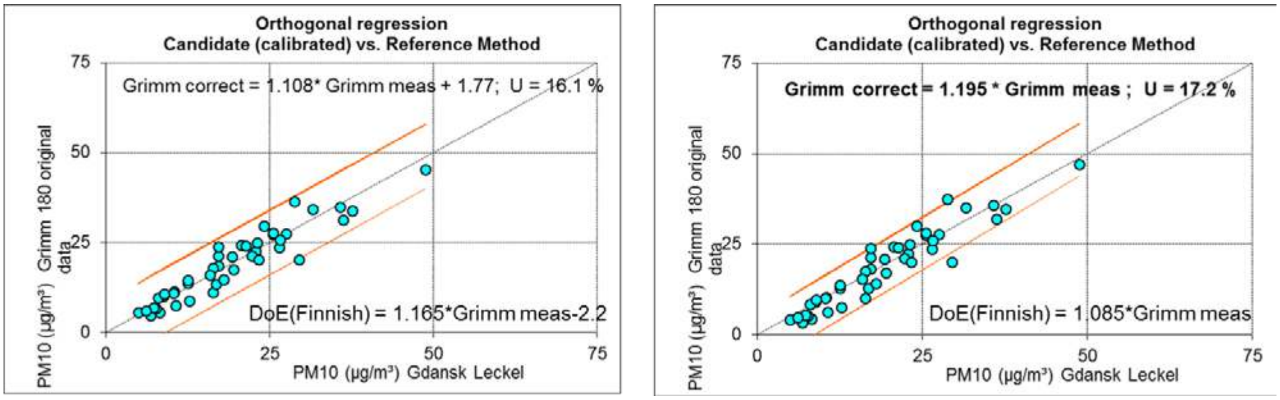


Figure 4.4. *Orthogonal regression analysis between the Grimm 180 and the reference method, see text in Figure 4.3.*

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.

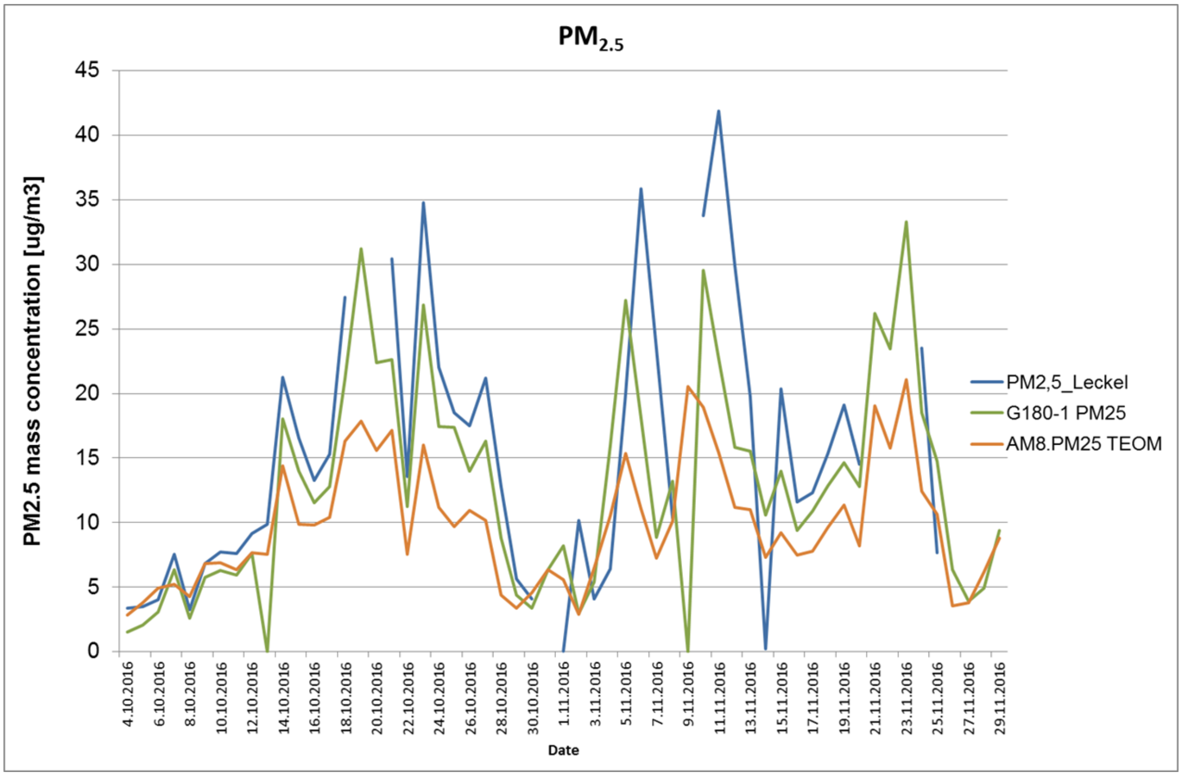


Figure 4.5. *The daily average values of $PM_{2.5}$ mass concentration for site analyzer TEOM 1400ab, optical analyzer by Grimm and the reference method at station AM8 in Gdansk.*

The hourly average values of $PM_{2.5}$ 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.

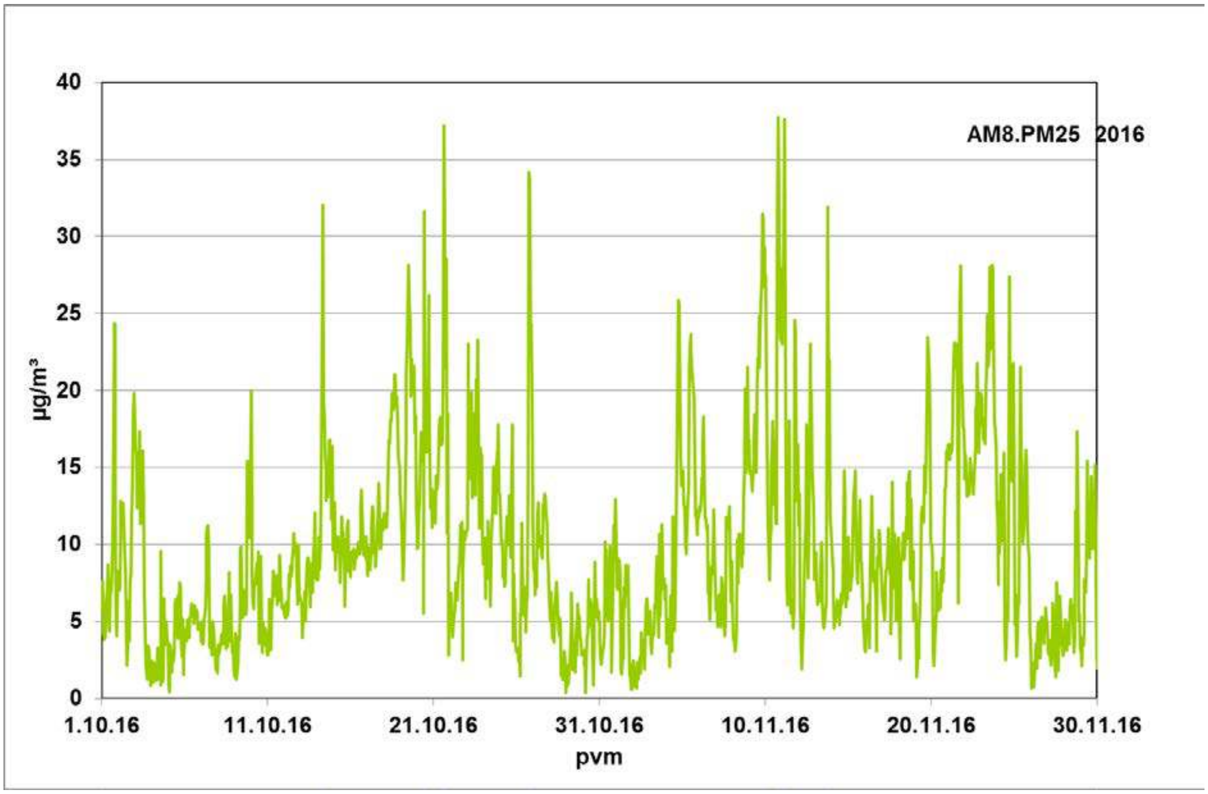


Figure 4.6. *Hourly averages for $PM_{2.5}$ mass concentration measured by site analyzer TEOM 1400ab at AM8, Gdansk.*

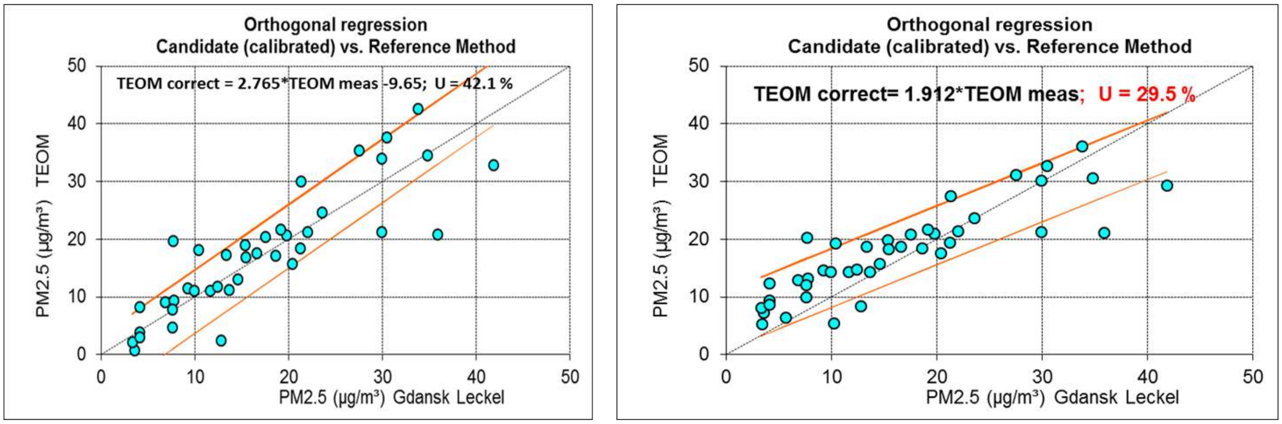


Figure 4.7. *Orthogonal regression analysis between the site analyzer for $PM_{2.5}$ at AM8 and the reference method, see text in Figure 4.3.*

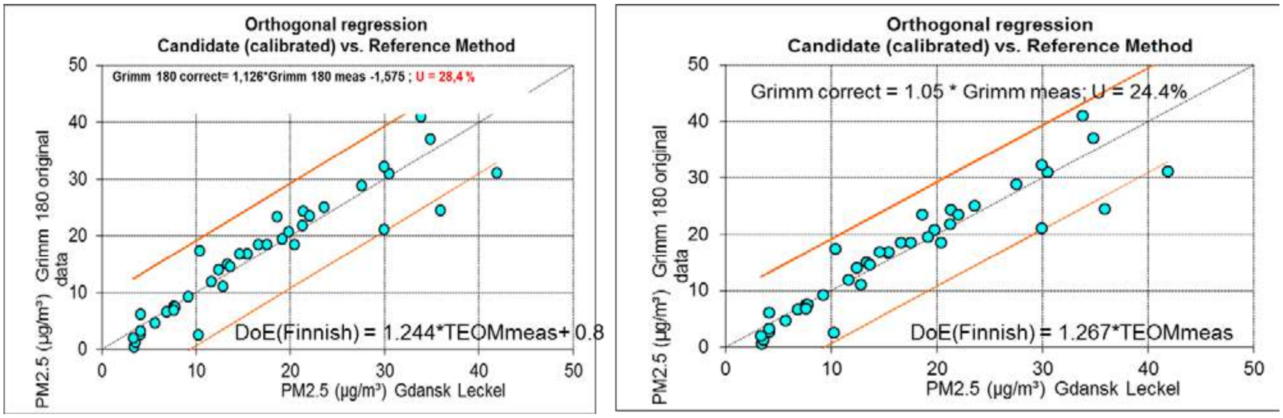


Figure 4.8. *Orthogonal regression analysis between the Grimm 180 and the reference method, see text in Figure 4.3.*

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.

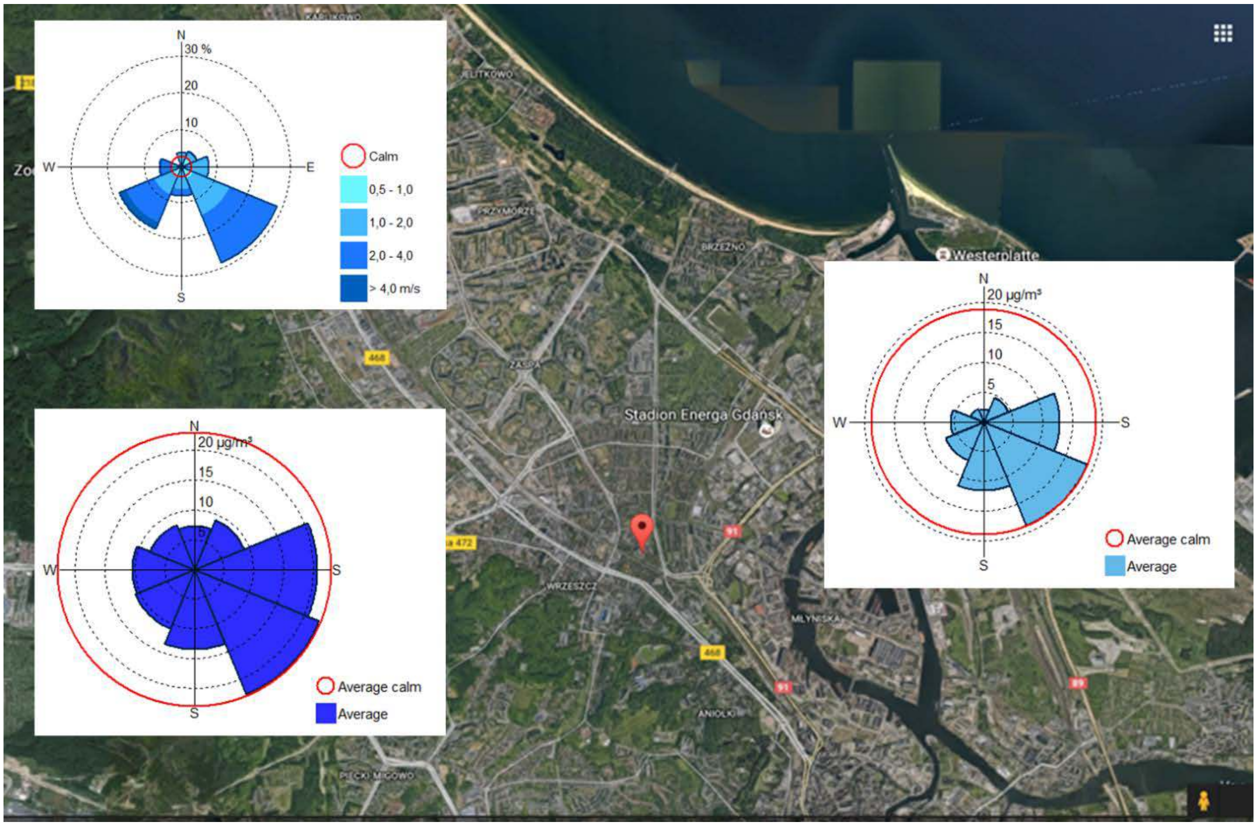


Figure 4.9. *Pollution roses for the wind speed, mass concentration of PM_{10} and $PM_{2.5}$ at station AM8.*

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.

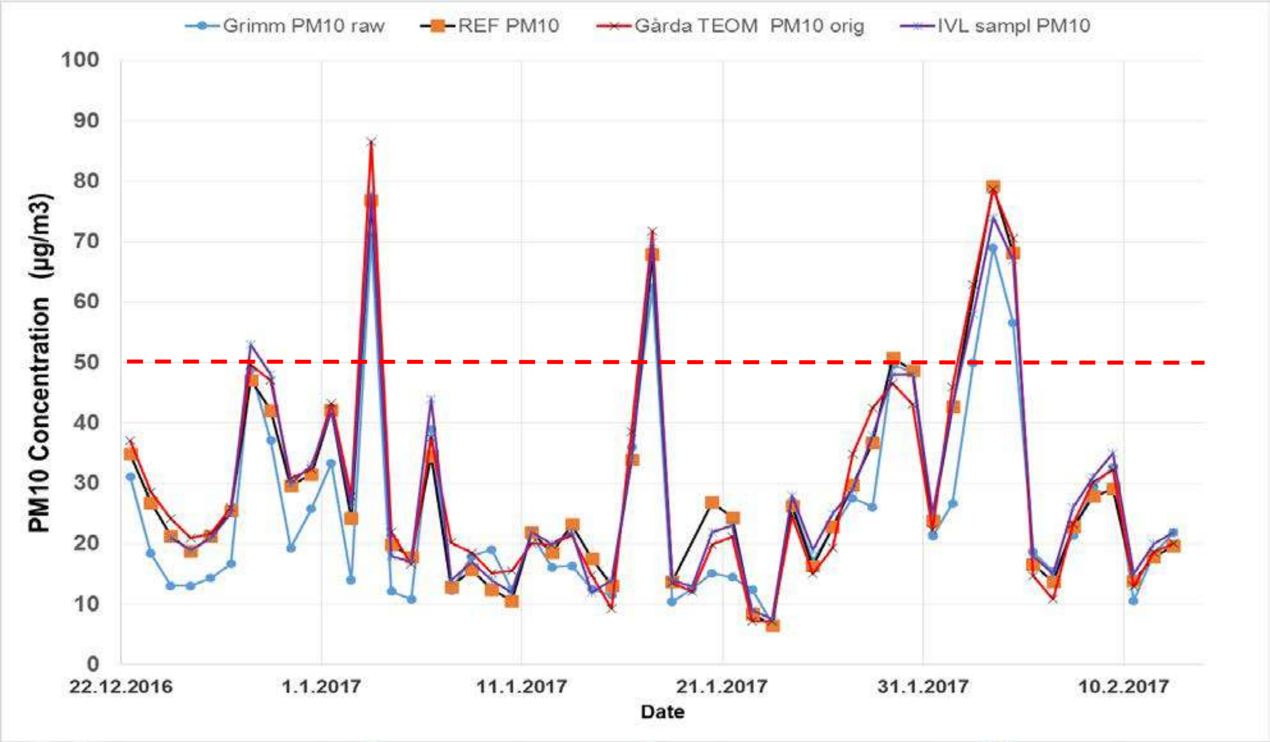


Figure 4.10. *The daily average values of PM_{10} mass concentration for site analyzer TEOM 1400ab, optical analyzer Grimm 180, IVL PM_{10} sampler, and the reference method at station Gårda in Gothenburg.*

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.

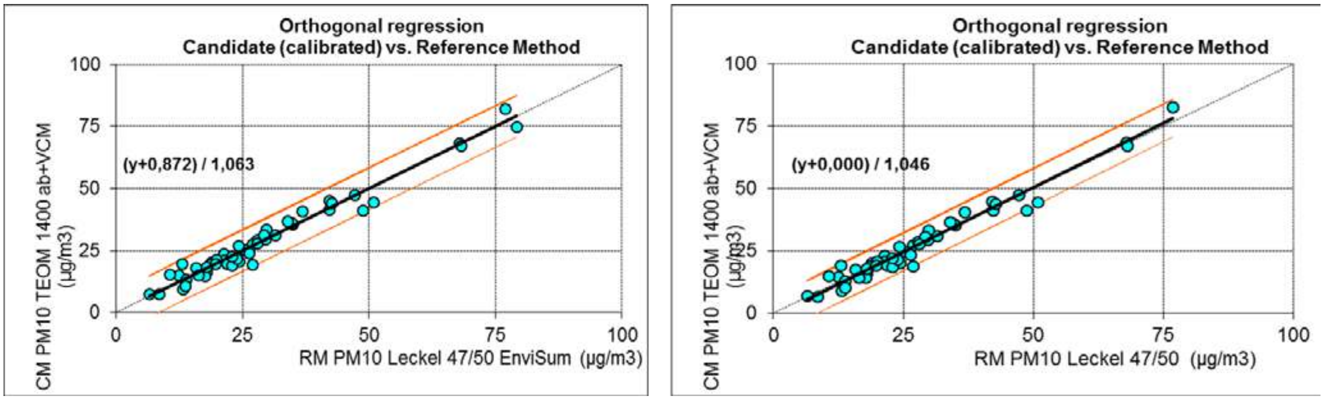


Figure 4.11. *Orthogonal regression analysis between the site analyzer TEOM 1400ab for* PM_{10} *at Gårda station and the reference method, see text in Figure 4.3.*

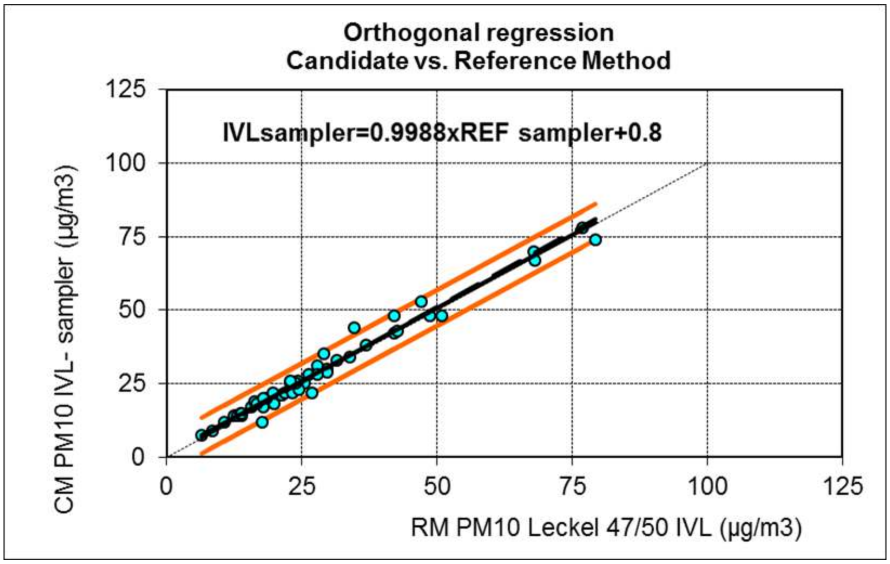


Figure 4.12. *Orthogonal regression analysis between the IVL sampler for* PM_{10} *and the reference method. The relationship between the IVL sampler and the reference sampler is shown in the figure.*

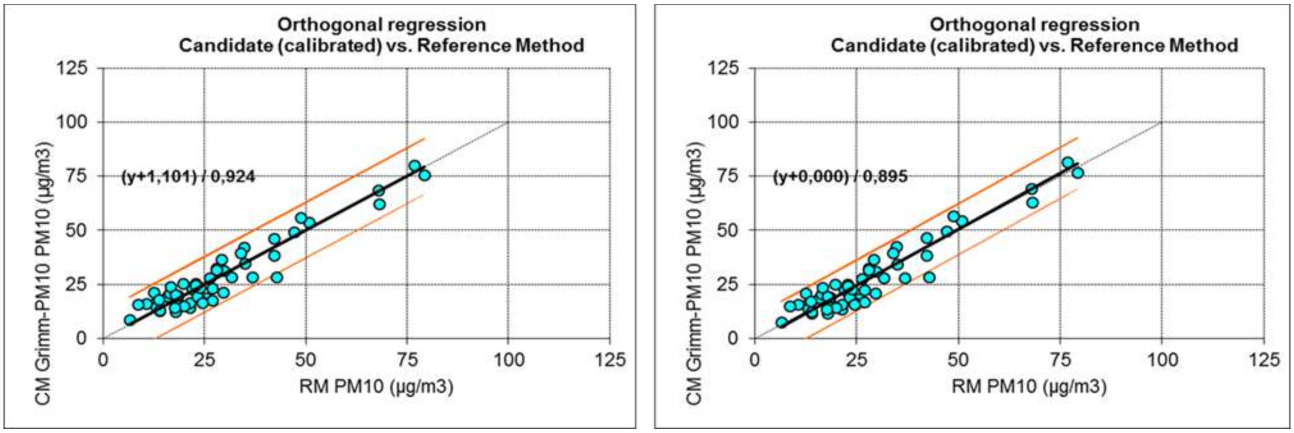


Figure 4.13. *Orthogonal regression analysis between the Grimm 180 and the reference method, see text in Figure 4.3.*

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$_{10}$	**Criteria**	**Gårda: TEOM 1400ab+VCM**	**IVL sampler**	**Grimm 180**
Concentration range	**$\mu g/m^3$**	**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.

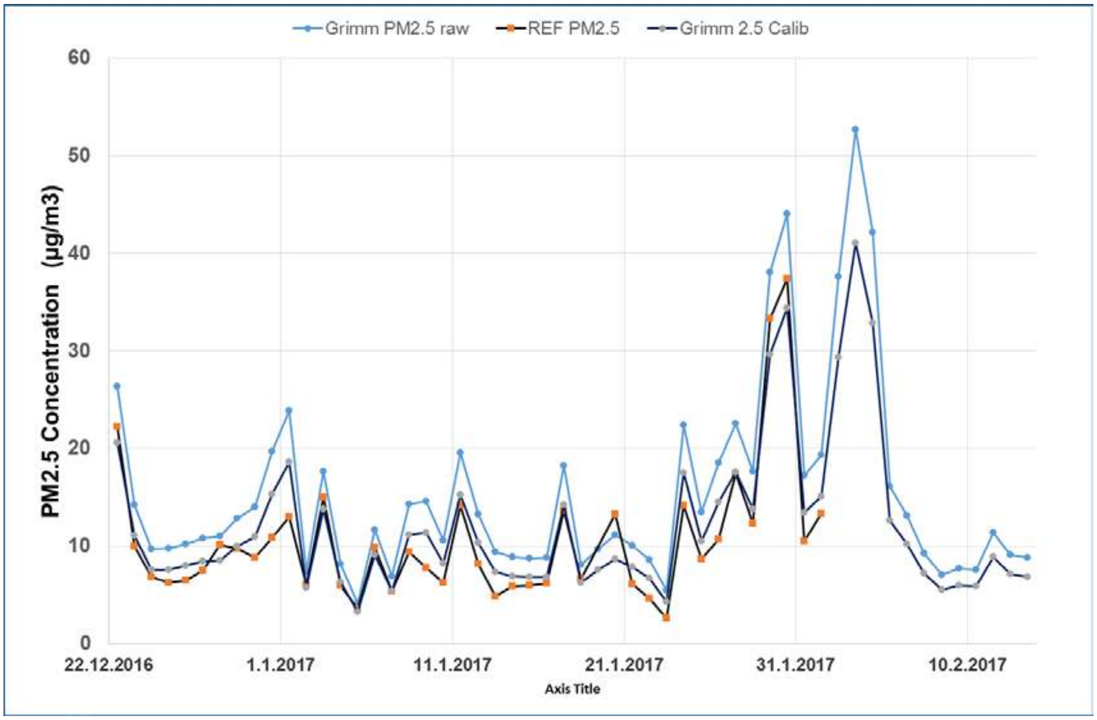


Figure 4.14. *The daily average values of $PM_{2.5}$ mass concentration for optical analyzer Grimm 180, and the reference method at station Gårda in Gothenburg. Grimm $PM_{2.5}$ raw means that the results is not corrected by any calibration factor, while results are corrected with the calibration function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

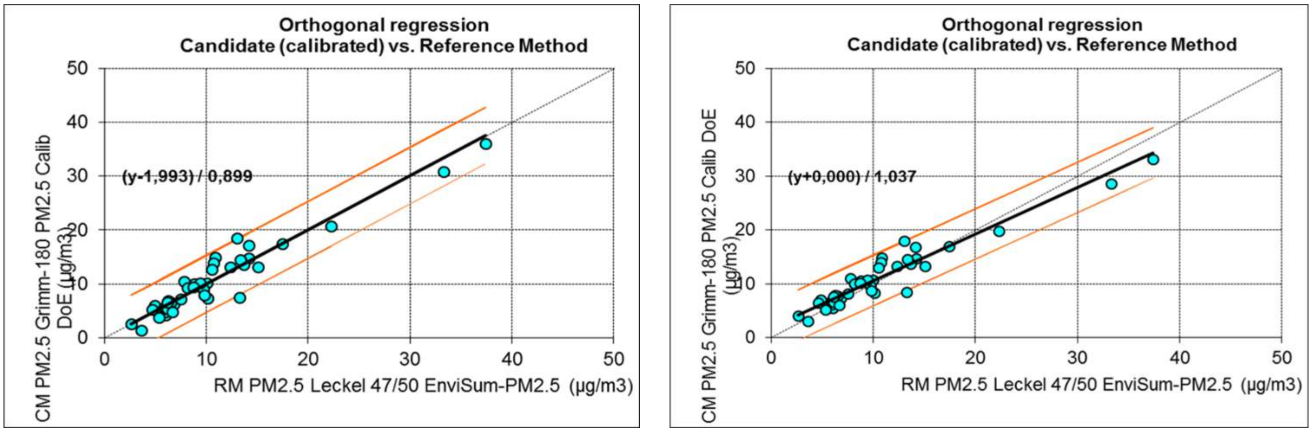


Figure 4.15. *Orthogonal regression analysis between the Grimm 180 (corrected by calibration) and the reference method for $PM_{2.5}$, see text in Figure 4.3.*

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

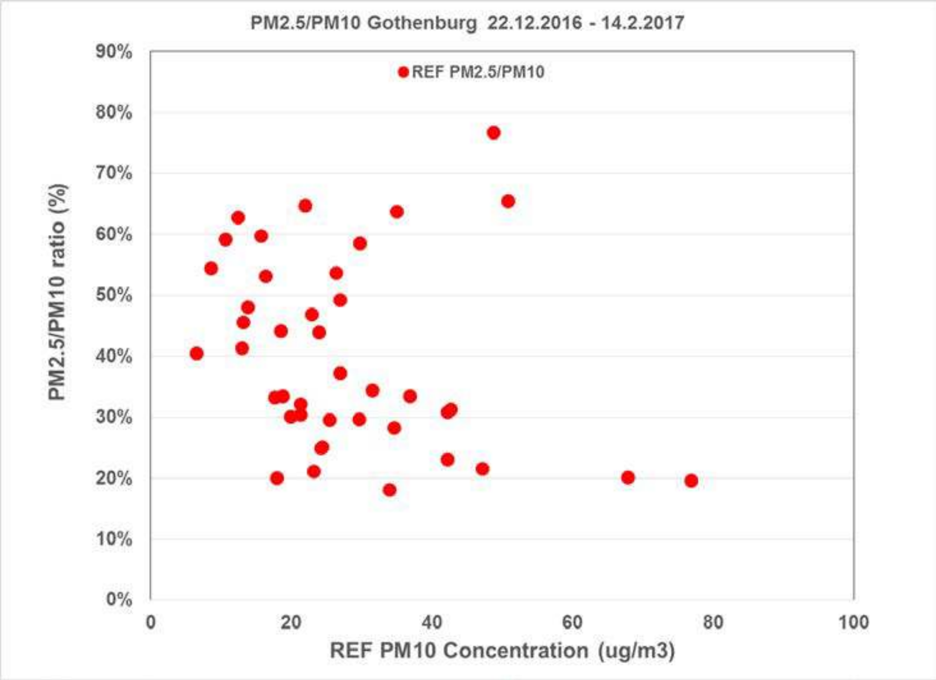


Figure 4.16. *The ratio of $PM_{2.5}/PM_{10}$ calculated from the Reference method.*

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.

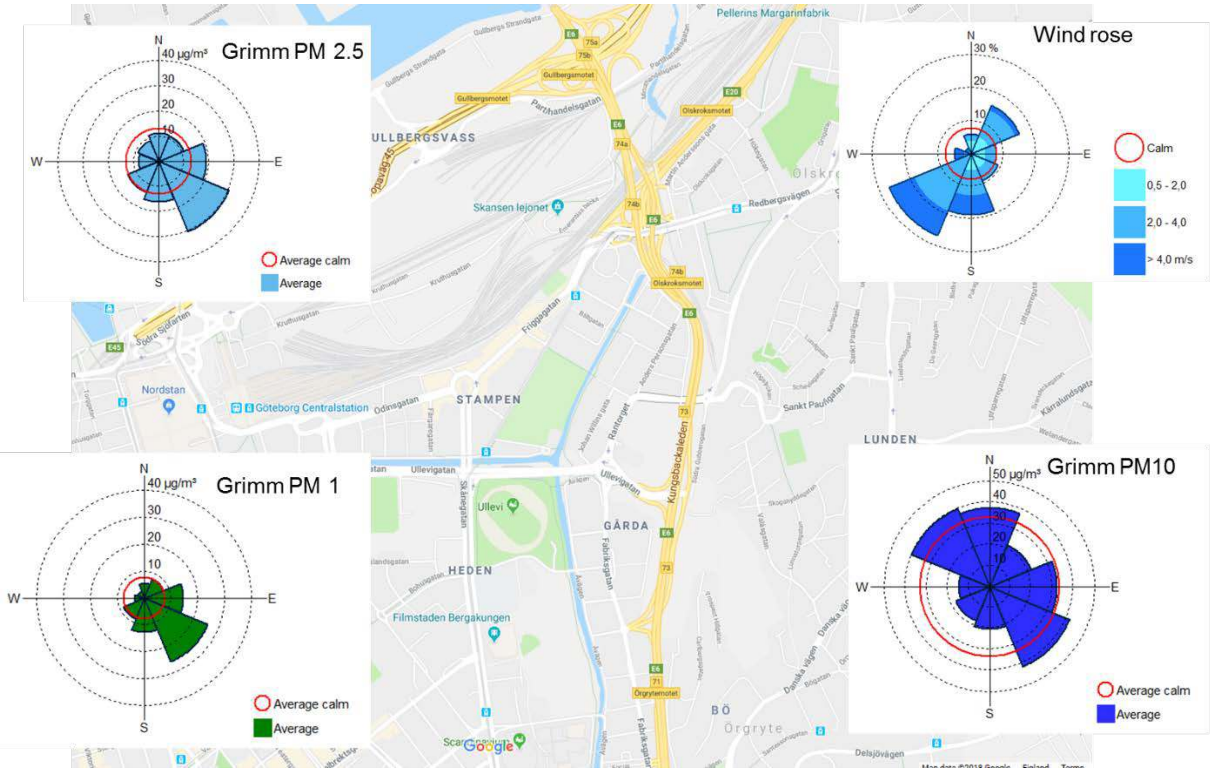


Figure 4.17. *Wind and pollution roses for the wind speed, mass concentration of PM_{10} and $PM_{2.5}$ at station Gårda.*

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.

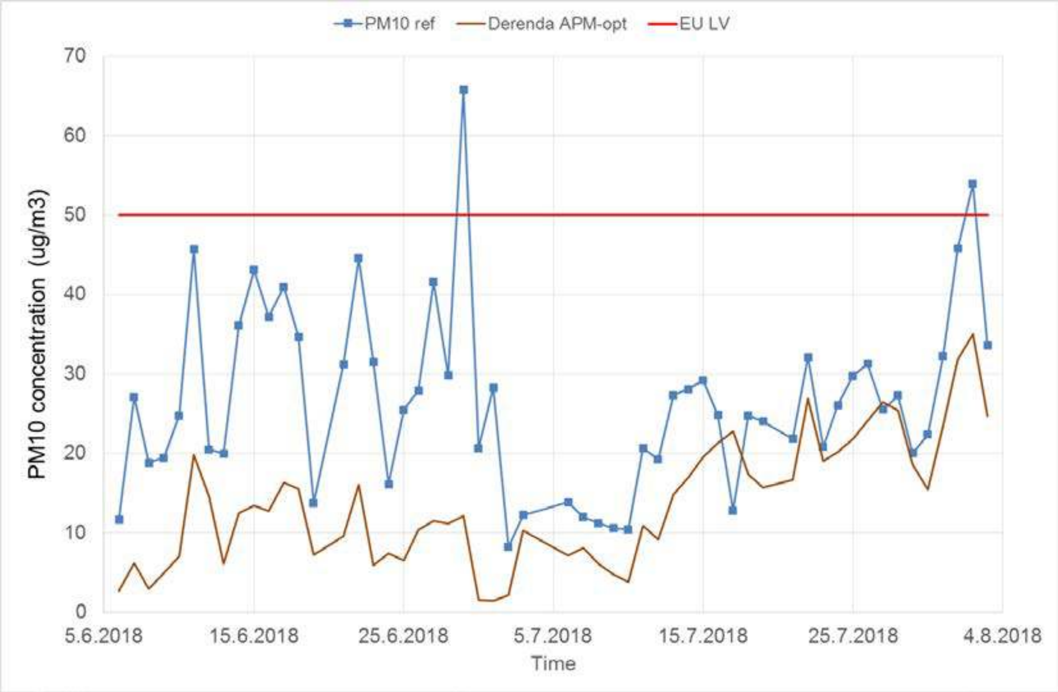


Figure 4.18. *The daily average values of PM_{10} mass concentration for site analyzer APM2 optical method and the APM2 filter method as the reference method at station No. 4 in St. Petersburg. Red line represents the EU limit value of PM_{10} daily average concentration.*

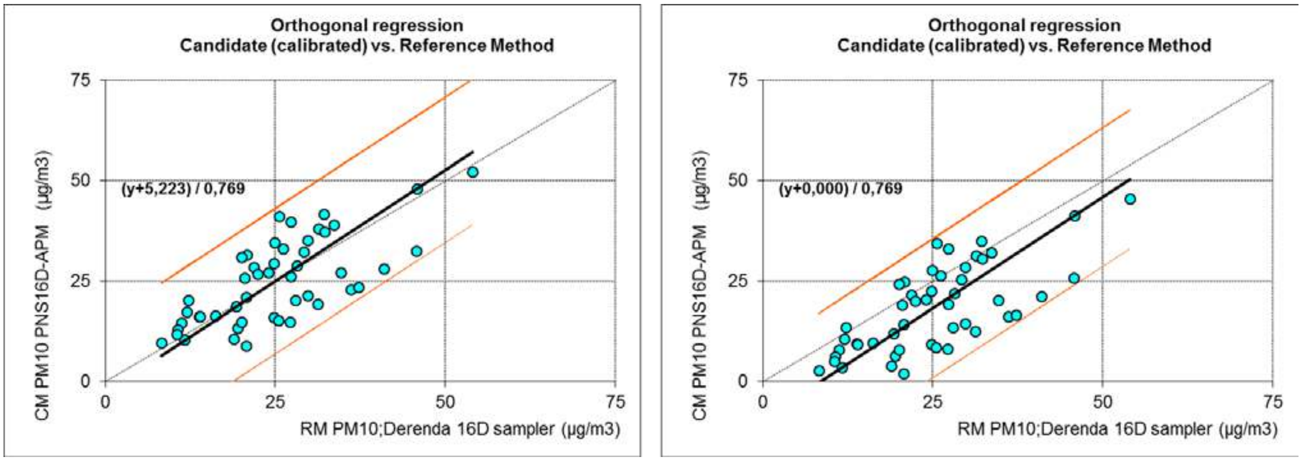


Figure 4.19. *Orthogonal regression analysis between the APM optical method and the APM filter sampling as reference method for PM_{10}, see text in Figure 4.3 except that in the figure right the slope is not forced through the origin.*

In Figure 4.20, the time series of daily averages for the $PM_{2.5}$ 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.

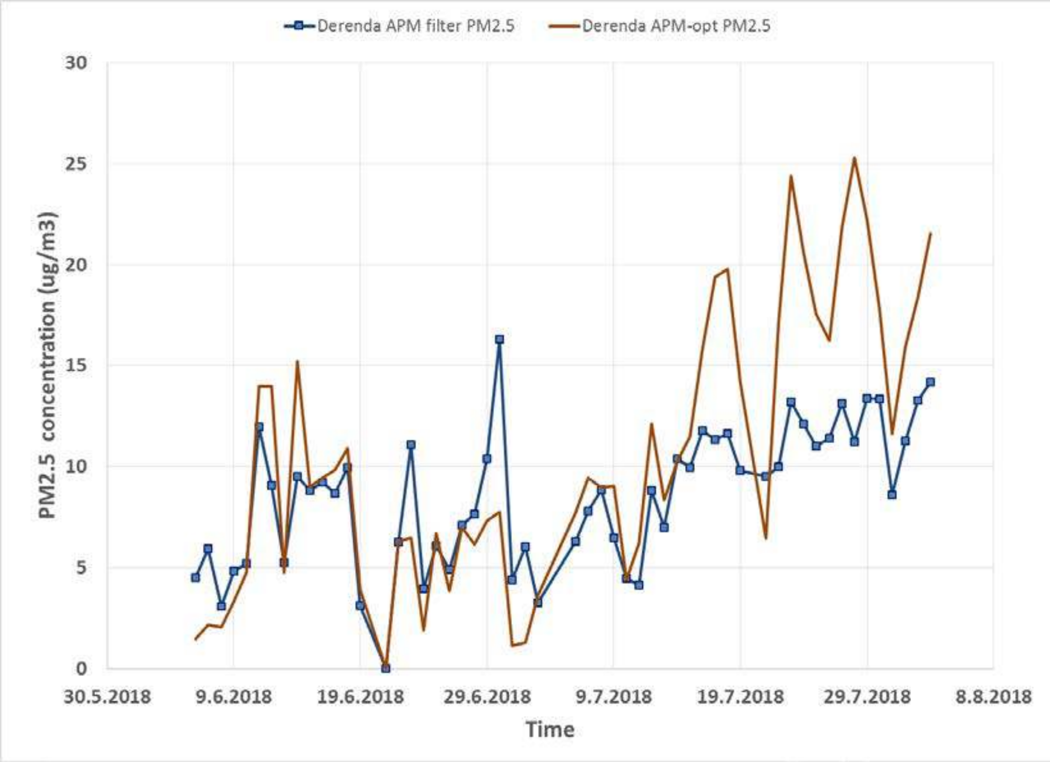


Figure 4.20. *The daily average values of PM$_{2.5}$ mass concentration for site analyzer APM2 optical method and the APM2 filter method as the reference method at station No. 4 in St. Petersburg.*

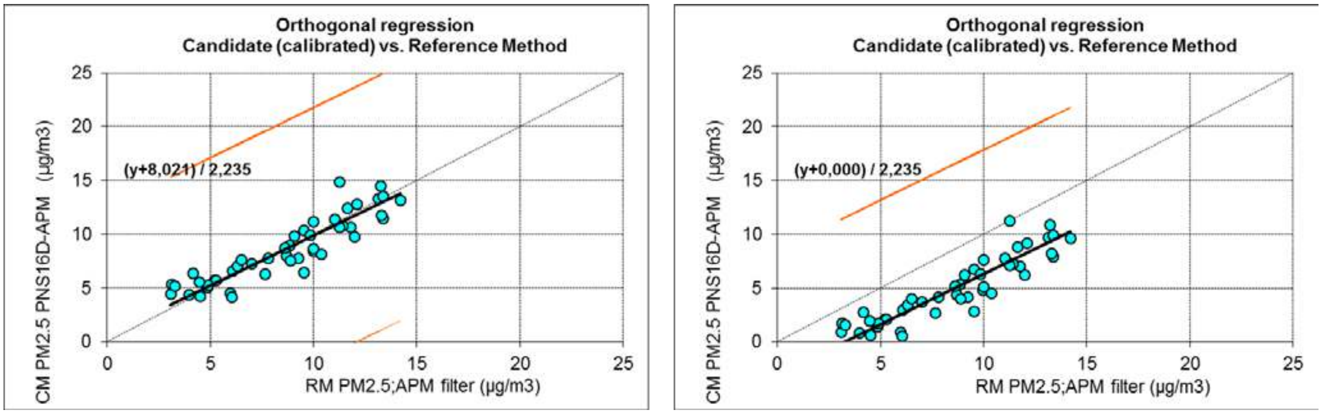


Figure 4.21. *Orthogonal regression analysis between the APM optical method and the APM filter sampling as reference method for PM$_{2.5}$, see text in Figure 4.3 except that in the figure right the slope is not forced through the origin.*

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.

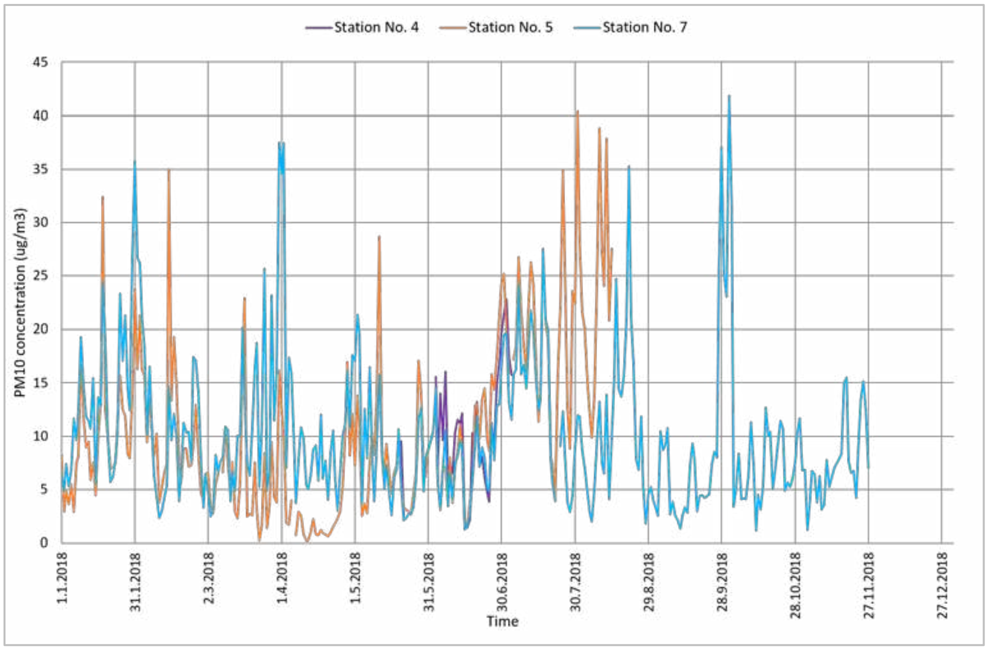


Figure 4.22. *The daily average values of PM_{10} concentration at stations No. 4, No. 5 and No. 7 in 2018.*

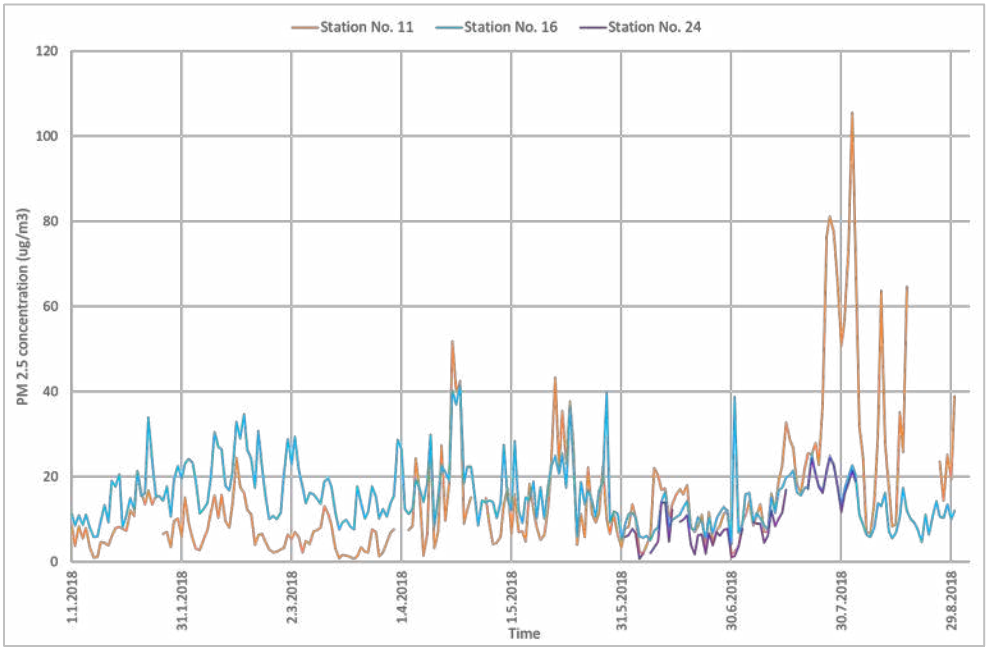


Figure 4.23. *The daily average values of $PM_{2.5}$ concentration at stations No. 11, No. 16 and No. 24 in January–August 2018.*

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).

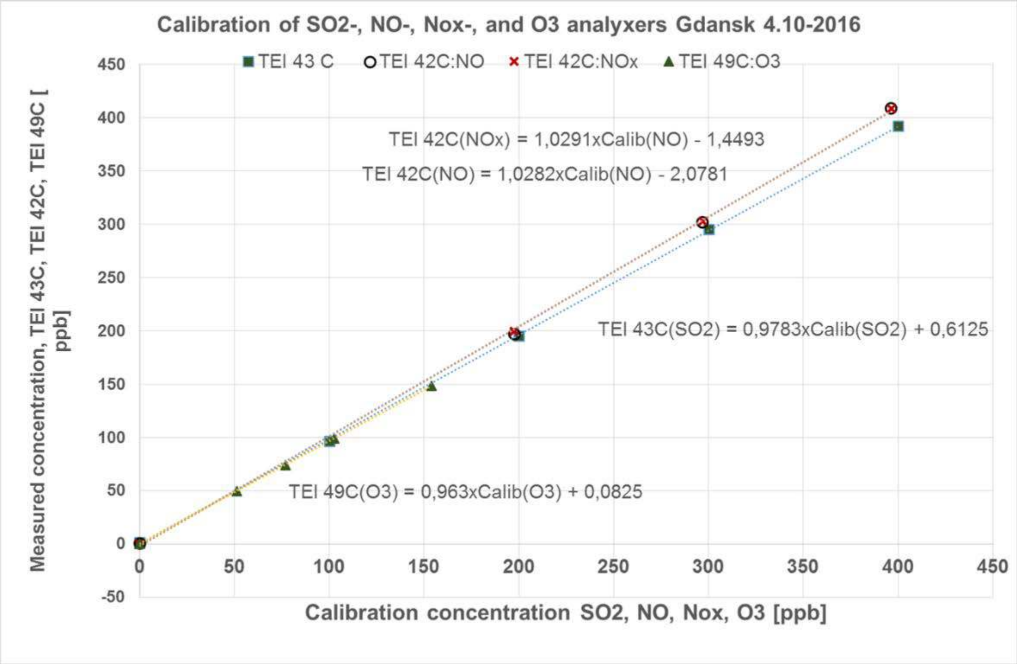


Figure 4.24. *Calibration of the SO_2, NO and O_3 analyzers at station AM8 in Gdansk. The calibration concentrations are shown in x-axis while the output concentrations of the station analyzers are in y-axis. The regression equations for each of the analyzers are shown in the figure beside the regression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

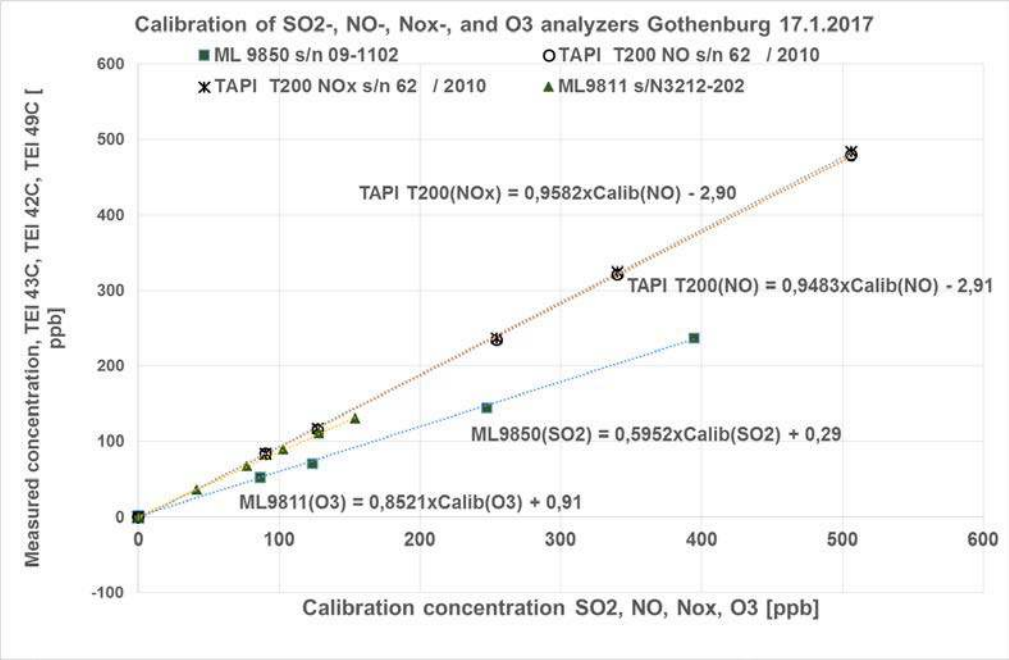


Figure 4.25. Calibration of the SO_2, NO and O_3 analyzers at station Femman in Gothenburg. The calibration concentrations are shown in x-axis while the output concentrations of the station analyzers are shown in y-axis. The regression equations for each of the analyzers are shown in the figure beside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

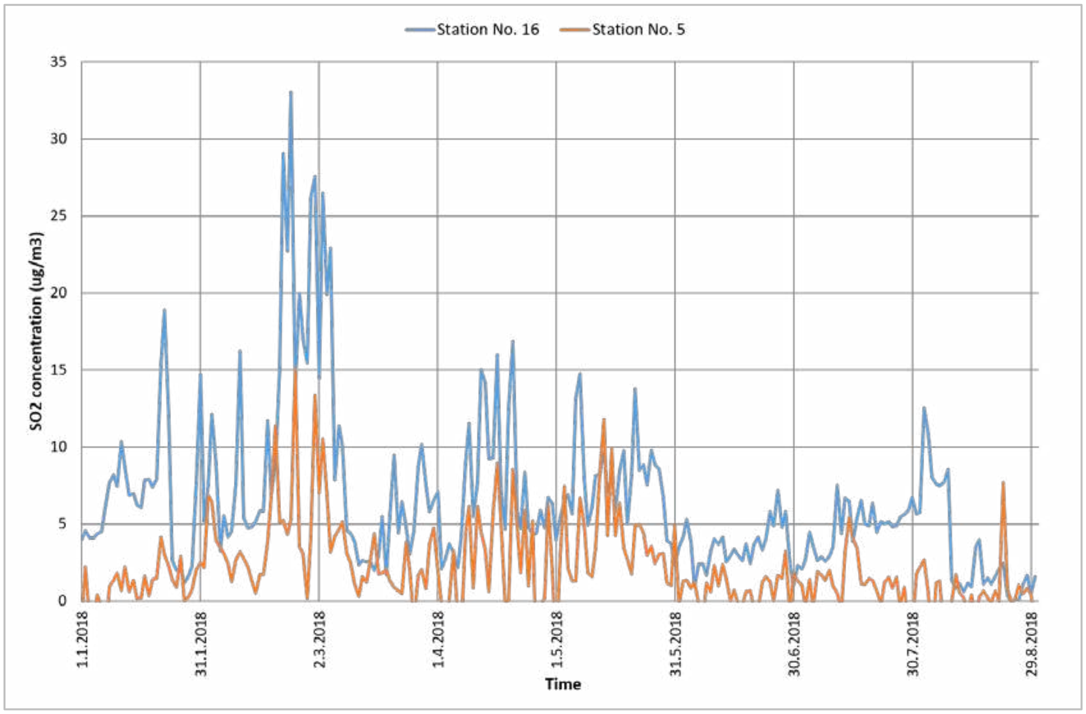


Figure 4.26. *The daily average values of SO_2 concentration at stations No. 5 and No. 16 in St. Petersburg in January–August 2018.*

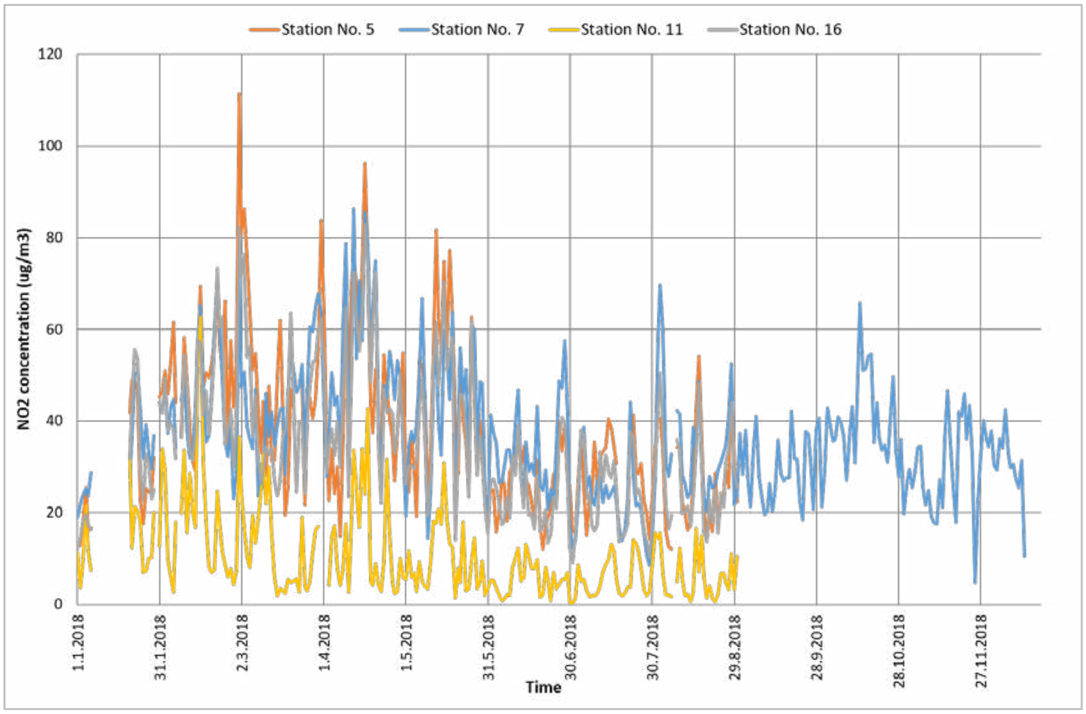


Figure 4.27. *The daily average values of NO_2 concentration at stations No. 5, No. 7, No. 11 and No. 16 in St. Petersburg in 2018.*

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
O3	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_{10} and $PM_{2.5}$ measurements were conducted at station AM8. In case of PM_{10} 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 (µg/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 EN-standards 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).

References

ACES Report 4, 2012. Equivalence of PM10 Instruments at a Road Traffic Site – A Study in Stockholm Spring 2012. Compiled by H. Areskoug. Stockholm University.

Beijk R., Hoogerbrugge R., Hafkenscheid T.L., Arkel F.T. van, Stefess G.C., Meulen A. van der, Wesseling J.P., Sauter F.J., Albers R.A.W., 2006. PM_{10}: Validatie en equivalentie 2006. RIVM rapport 680708001/2007, (www.rivm.nl)

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).

EN ISO/IEC 17025:2005. General requirements for the competence of testing and calibration laboratories.

Ferm M., Gudmundsson A., Persson K., 2001. Measurements of PM10 and PM2.5 within the Swedish urban network. Proc. from NOSA Aerosol Symposium Lund, Sweden 8-9 Nov.

LUBW, 2005. Prüfung des Schwebstaubmessgerätes Environmental Dust Monitor – Model 180 der Firma Grimm Aerosol-Technik auf Gleichwertige Ergebnisse wie mit der Referenzmethode der Europäischen Norm din/en 12341 bei der Messung von Schwebstaub der Fraktion PM10. LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, Bericht-Nr. 21-18/2005, Germany.

Waldén J., Hillamo R., Aurela M., Mäkelä T., Laurila S., 2010. Demonstration of the equivalence of PM2.5 and PM10 measurement methods in Helsinki 2007–2008. 103 pp. Finnish Meteorological Institute, Studies 3, Helsinki.

Waldén J., Waldén T., Laurila S., Hakola H., 2017. Demonstration of the equivalence of $PM_{2.5}$ and PM_{10} 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_2, CO, O_3, PM_{10} & $PM_{2.5}$

Equipment: PM_{10}/PM2.5 samplers: Leckel SEQ-47-50, sequential PM reference sampler

Continuous PM analyzer: Grimm 180 (PM_{10}-$PM_{2.5}$-PM_1)

Dilution device: Teledyne T700: Calibration ranges:

-NO: 0 – 500 ppb	Gas standard: NO in N_2: C = 20 ppm; U=±1%
-SO_2: 0 – 250 ppb	Gas standard: SO_2 in N_2: C = 10 ppm; U=±1%
-CO: 0 – 10 ppm	Gas standard: CO in Synthetic air: C = 1000 ppm; U=±1%

Gas standards: NO, SO_2, 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_{10} & $PM_{2.5}$) 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

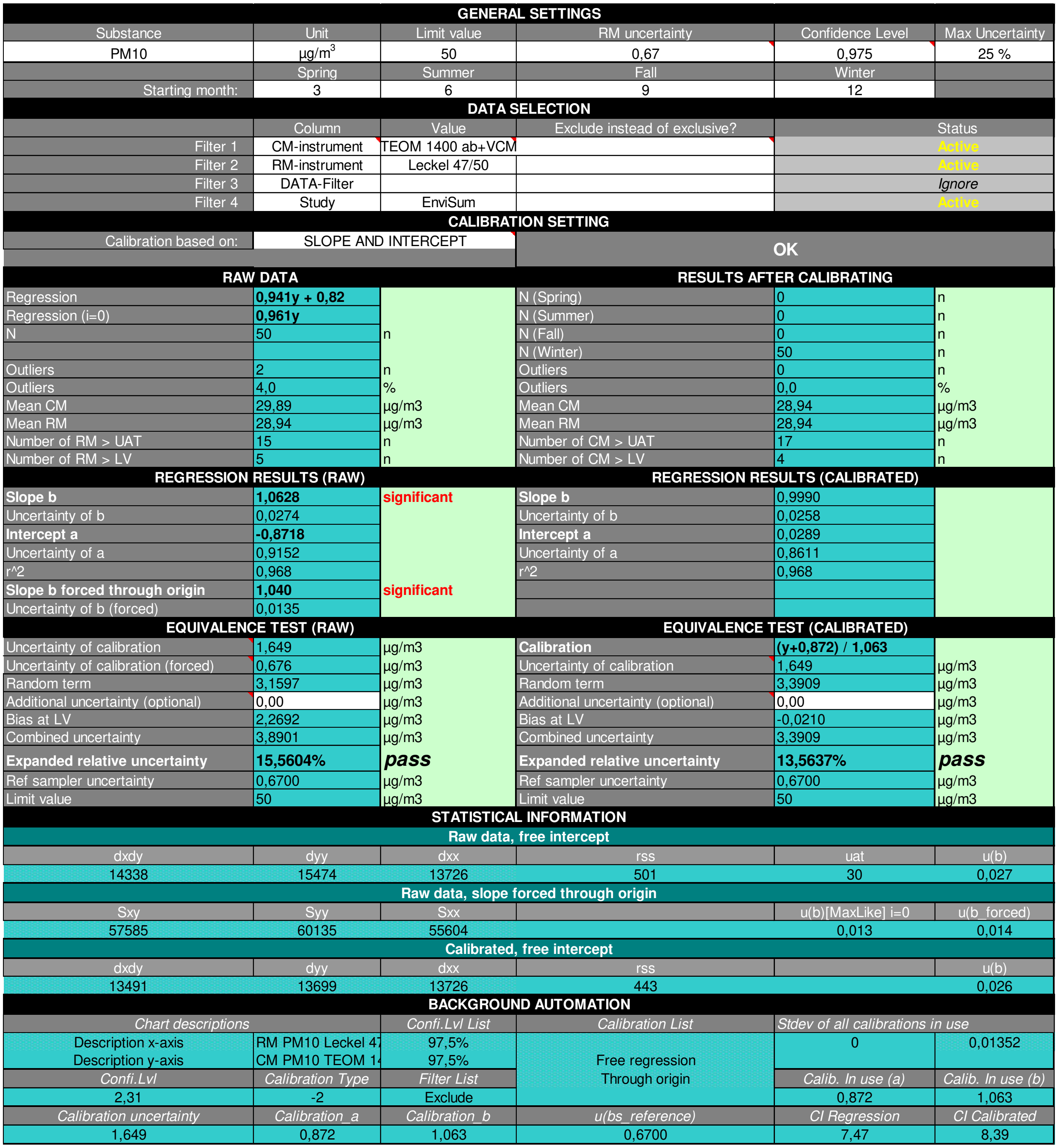
MINERAL:

- 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_2 range: 0 – 250 ppb
- NO: 0 – 500 ppb
- CO: 0 – 10 ppm
- O_3: 0 – 200 ppb

Annex 2. Equivalent test results

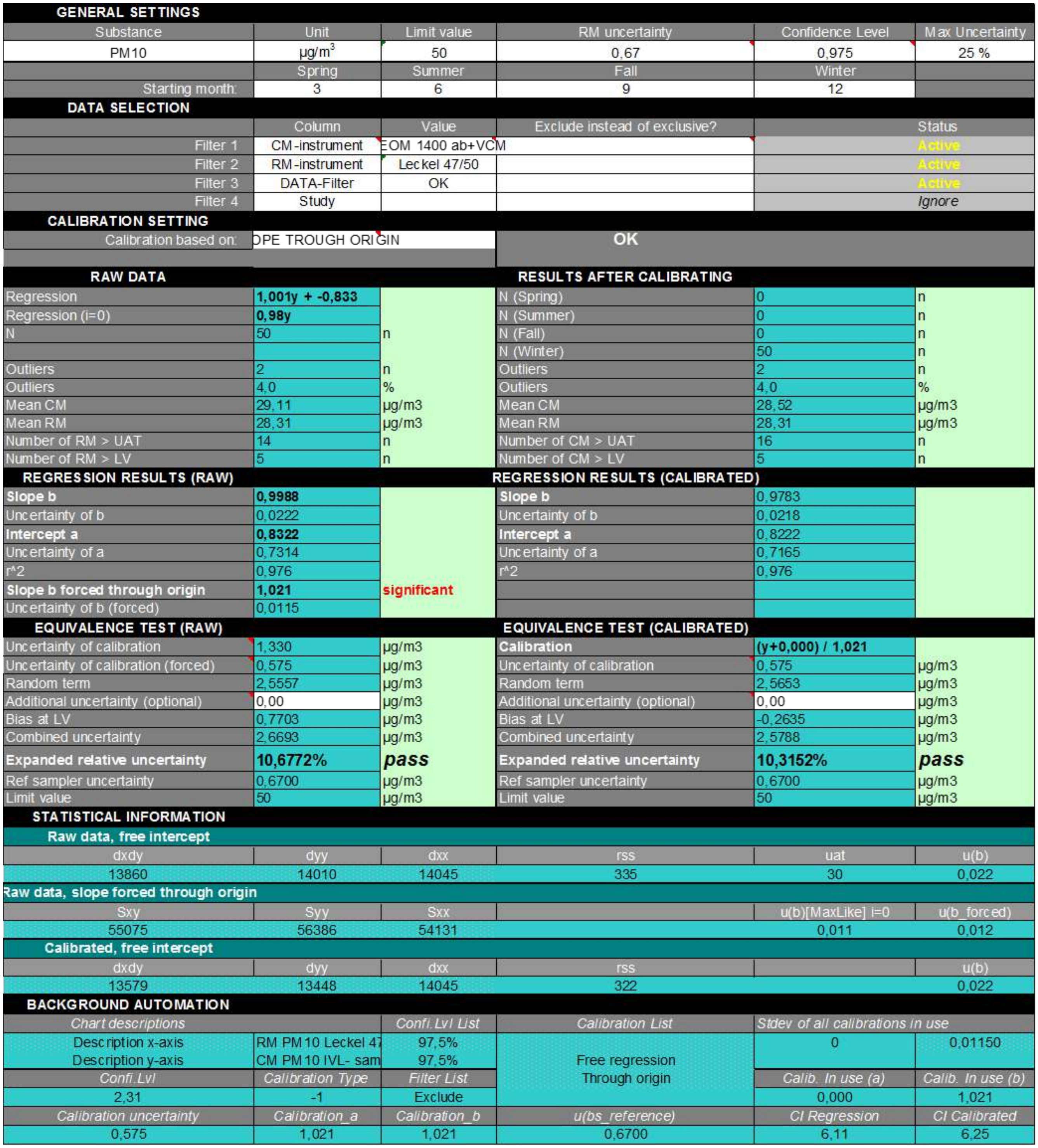
TEOM 1400ab

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



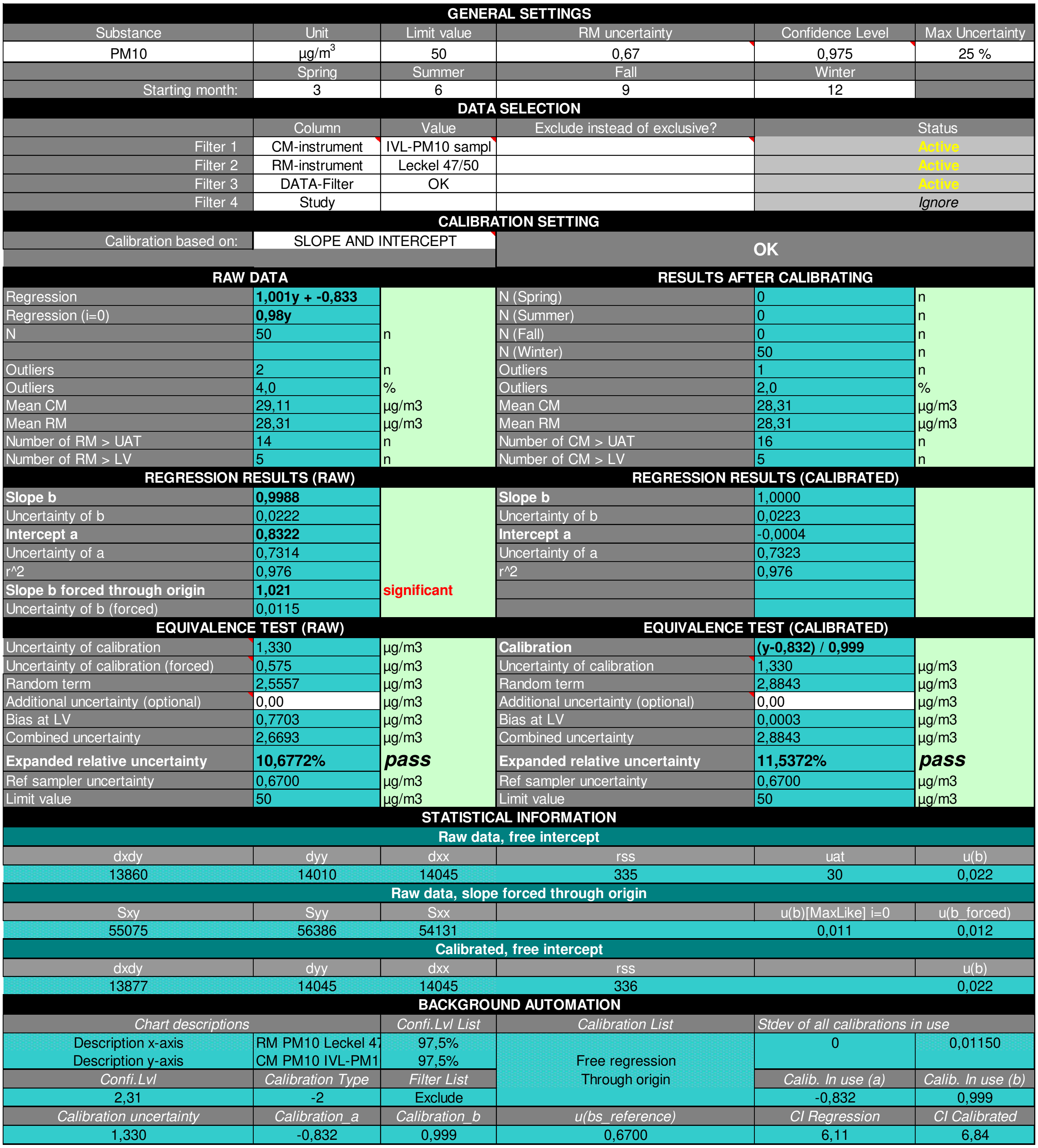
GENERAL SETTINGS					
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	µg/m^3	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
DATA SELECTION					
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	TEOM 1400 ab+VCM			Active
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter				*Ignore*
Filter 4	Study	EnviSum			Active
CALIBRATION SETTING					
Calibration based on:	SLOPE AND INTERCEPT		**OK**		
RAW DATA			**RESULTS AFTER 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
REGRESSION RESULTS (RAW)			**REGRESSION RESULTS (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				
EQUIVALENCE TEST (RAW)			**EQUIVALENCE 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
STATISTICAL 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
BACKGROUND AUTOMATION					
Chart descriptions		*Confi.Lvl List*	*Calibration List*	*Stdev of all calibrations in use*	
Description x-axis	RM PM10 Leckel 47	97,5%	Free regression	0	0,01352
Description y-axis	CM PM10 TEOM 14	97,5%	Through origin		
Confi.Lvl	*Calibration Type*	*Filter List*		*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*	*CI 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.



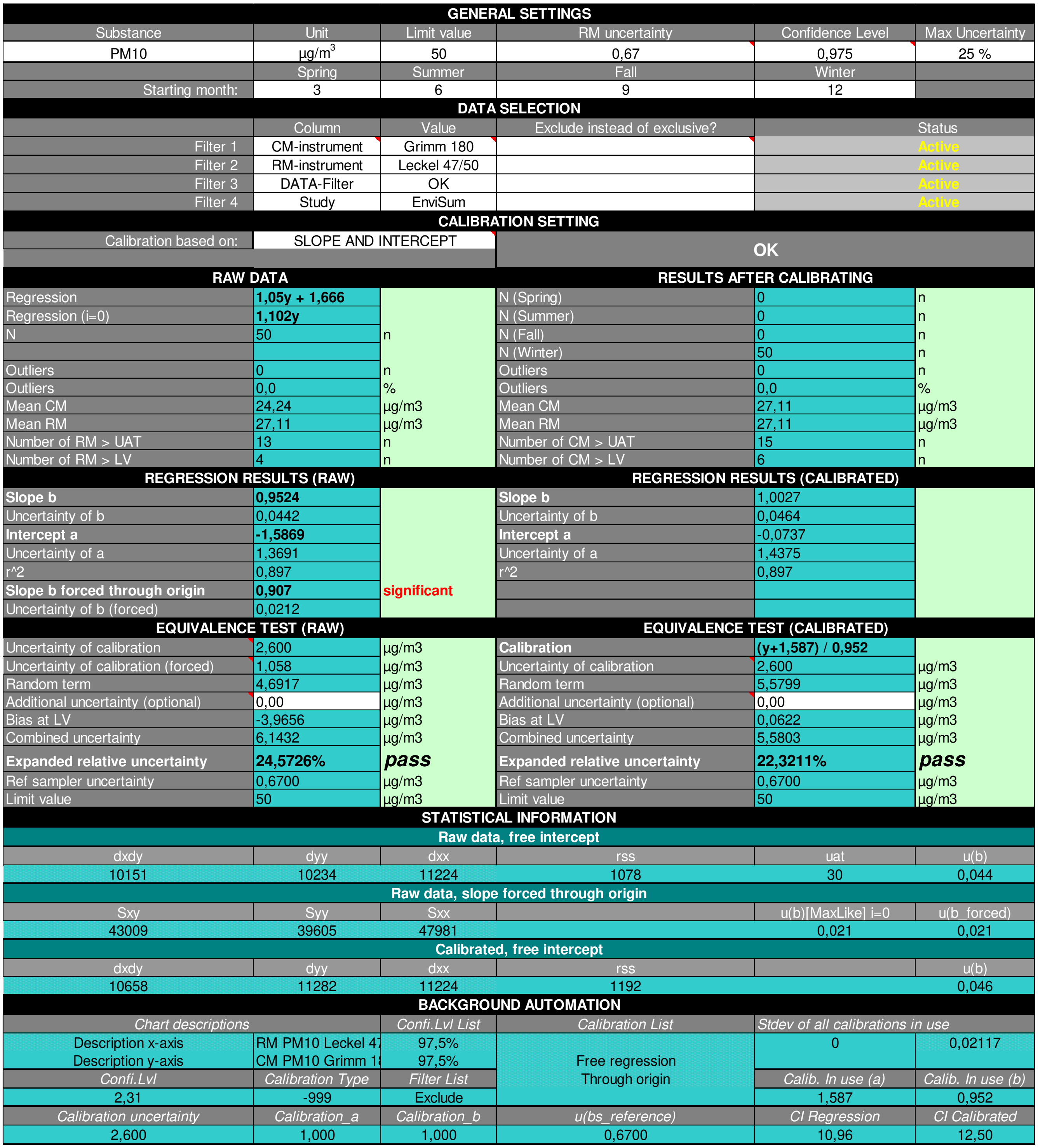
GENERAL SETTINGS					
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	µg/m^3	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
DATA SELECTION					
	Column	Value	Exclude instead of exclusive?		Status
Filter 1	CM-instrument	EOM 1400 ab+VCM			Active
Filter 2	RM-instrument	Leckel 47/50			Active
Filter 3	DATA-Filter	OK			Active
Filter 4	Study				*Ignore*
CALIBRATION SETTING					
Calibration based on:	OPE TROUGH ORIGIN		**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 (CALIBRATED)**		
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					
dxdy	dyy	dxx	rss	uat	u(b)
13860	14010	14045	335	30	0,022
Raw data, slope forced through origin					
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
55075	56386	54131		0,011	0,012
Calibrated, free intercept					
dxdy	dyy	dxx	rss		u(b)
13579	13448	14045	322		0,022
BACKGROUND AUTOMATION					
Chart descriptions		*Confi.Lvl List*	*Calibration List*	*Stdev of all calibrations in use*	
Description x-axis	RM PM10 Leckel 47	97,5%		0	0,01150
Description y-axis	CM PM10 IVL- sam	97,5%	Free regression Through origin		
Confi.Lvl	*Calibration Type*	*Filter List*		*Calib. In use (a)*	*Calib. In use (b)*
2,31	-1	Exclude		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

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



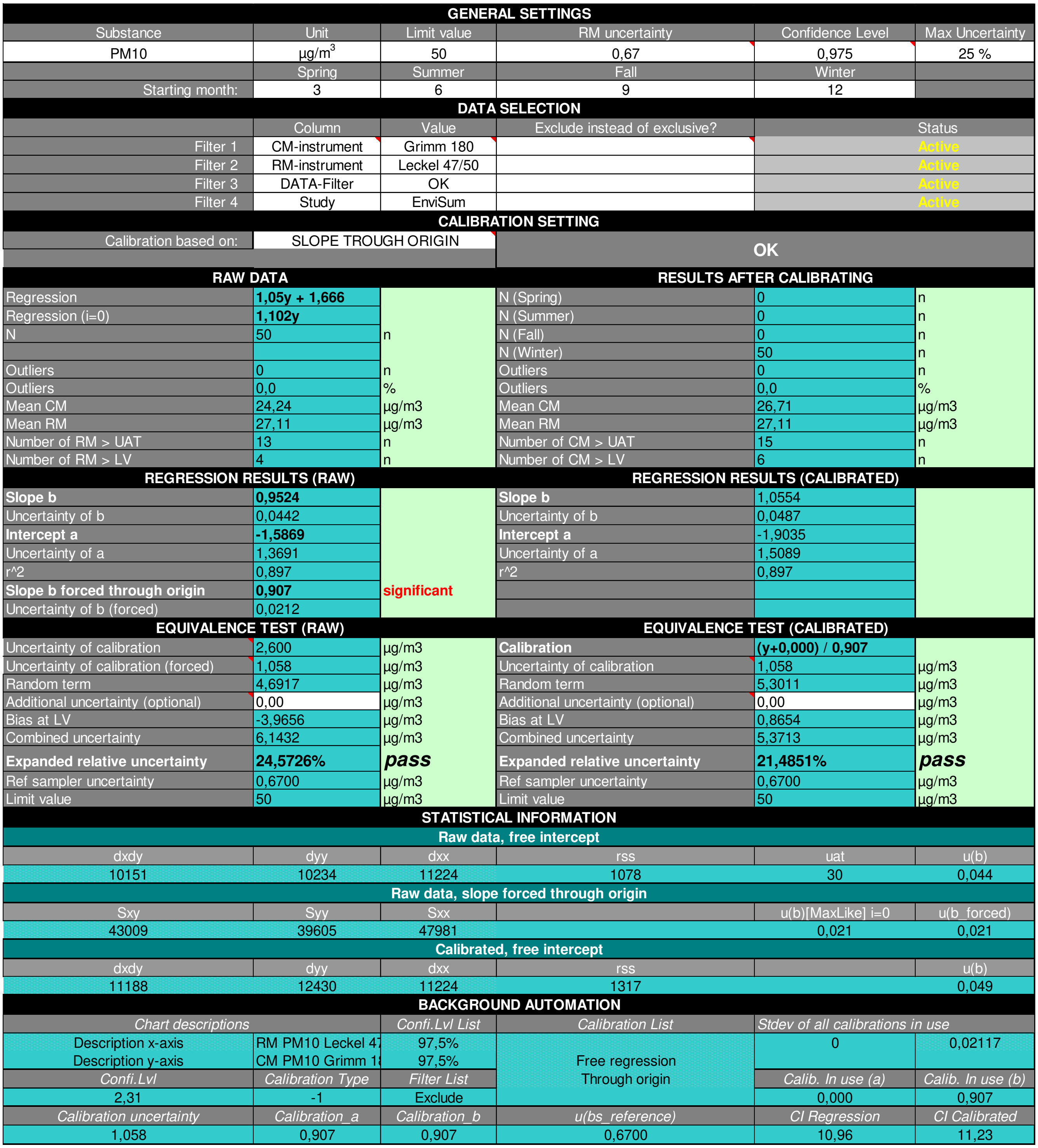
GENERAL SETTINGS					
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	µg/m^3	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
DATA SELECTION					
	Column	Value	Exclude instead of exclusive?	Status	
Filter 1	CM-instrument	IVL-PM10 sampl		Active	
Filter 2	RM-instrument	Leckel 47/50		Active	
Filter 3	DATA-Filter	OK		Active	
Filter 4	Study			*Ignore*	
CALIBRATION SETTING					
Calibration based on:	SLOPE AND INTERCEPT		**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	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	n
REGRESSION RESULTS (RAW)			**REGRESSION RESULTS (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 (RAW)			**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
STATISTICAL INFORMATION					
Raw data, free intercept					
dxdy	dyy	dxx	rss	uat	u(b)
13860	14010	14045	335	30	0,022
Raw data, slope forced through origin					
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
55075	56386	54131		0,011	0,012
Calibrated, free intercept					
dxdy	dyy	dxx	rss		u(b)
13877	14045	14045	336		0,022
BACKGROUND AUTOMATION					
Chart descriptions		*Confi.Lvl List*	*Calibration List*	*Stdev of all calibrations in use*	
Description x-axis	RM PM10 Leckel 47	97,5%	Free regression Through origin	0	0,01150
Description y-axis	CM PM10 IVL-PM1	97,5%			
Confi.Lvl	*Calibration Type*	*Filter List*		*Calib. In use (a)*	*Calib. In use (b)*
2,31	-2	Exclude		-0,832	0,999
Calibration uncertainty	*Calibration_a*	*Calibration_b*	*u(bs_reference)*	*CI Regression*	*CI Calibrated*
1,330	-0,832	0,999	0,6700	6,11	6,84

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



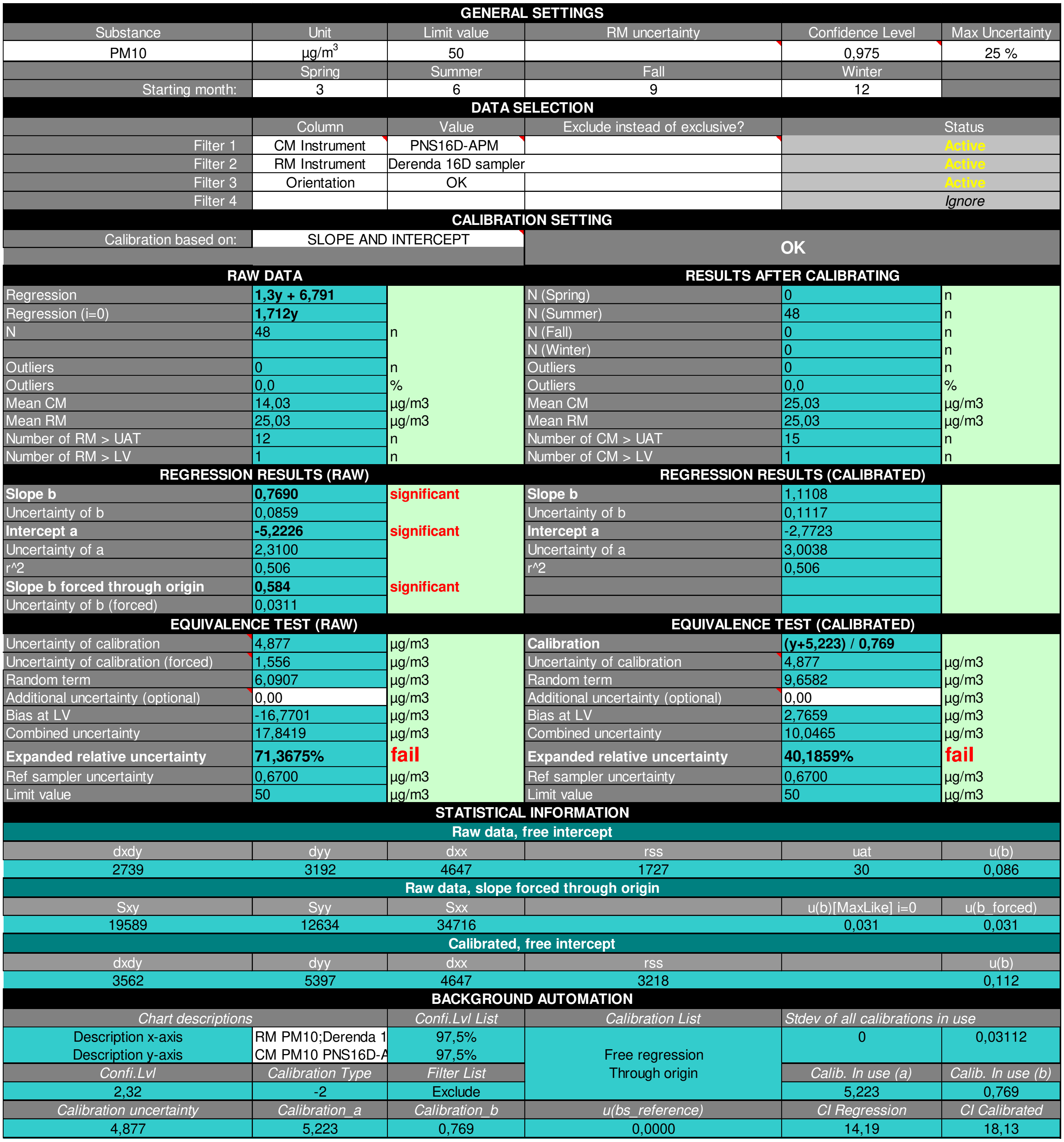
GENERAL SETTINGS					
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	µg/m^3	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
DATA SELECTION					
	Column	Value	Exclude instead of exclusive?	Status	
Filter 1	CM-instrument	Grimm 180		Active	
Filter 2	RM-instrument	Leckel 47/50		Active	
Filter 3	DATA-Filter	OK		Active	
Filter 4	Study	EnviSum		Active	
CALIBRATION SETTING					
Calibration based on:	SLOPE AND INTERCEPT		OK		
RAW DATA			RESULTS AFTER 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
			N (Winter)	50	n
Outliers	0	n	Outliers	0	n
Outliers	0,0	%	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 RESULTS (RAW)			REGRESSION RESULTS (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				
EQUIVALENCE TEST (RAW)			EQUIVALENCE 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	4,6917	µg/m3	Random term	5,5799	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	0,0622	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	0,6700	µg/m3
Limit value	50	µg/m3	Limit value	50	µg/m3
STATISTICAL INFORMATION					
Raw data, free intercept					
dxdy	dyy	dxx	rss	uat	u(b)
10151	10234	11224	1078	30	0,044
Raw data, slope forced through origin					
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
43009	39605	47981		0,021	0,021
Calibrated, free intercept					
dxdy	dyy	dxx	rss		u(b)
10658	11282	11224	1192		0,046
BACKGROUND AUTOMATION					
Chart descriptions		*Confi.Lvl List*	*Calibration List*	*Stdev of all calibrations in use*	
Description x-axis	RM PM10 Leckel 47	97,5%	Free regression Through origin	0	0,02117
Description y-axis	CM PM10 Grimm 18	97,5%			
Confi.Lvl	*Calibration Type*	*Filter List*		*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.



GENERAL SETTINGS					
Substance	Unit	Limit value	RM uncertainty	Confidence Level	Max Uncertainty
PM10	µg/m^3	50	0,67	0,975	25 %
	Spring	Summer	Fall	Winter	
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	
CALIBRATION SETTING					
Calibration based on:	SLOPE TROUGH ORIGIN		**OK**		
RAW DATA			**RESULTS AFTER 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
			N (Winter)	50	n
Outliers	0	n	Outliers	0	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
REGRESSION RESULTS (RAW)			**REGRESSION RESULTS (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	1,3691		Uncertainty of a	1,5089	
r^2	0,897		r^2	0,897	
Slope b forced through origin	**0,907**	**significant**			
Uncertainty of b (forced)	0,0212				
EQUIVALENCE TEST (RAW)			**EQUIVALENCE 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
STATISTICAL INFORMATION					
Raw data, free intercept					
dxdy	dyy	dxx	rss	uat	u(b)
10151	10234	11224	1078	30	0,044
Raw data, slope forced through origin					
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
43009	39605	47981		0,021	0,021
Calibrated, free intercept					
dxdy	dyy	dxx	rss		u(b)
11188	12430	11224	1317		0,049
BACKGROUND AUTOMATION					
Chart descriptions		*Confi.Lvl List*	*Calibration List*	*Stdev of all calibrations in use*	
Description x-axis	RM PM10 Leckel 47	97,5%	Free regression Through origin	0	0,02117
Description y-axis	CM PM10 Grimm 1	97,5%			
Confi.Lvl	*Calibration Type*	*Filter List*		*Calib. In use (a)*	*Calib. In use (b)*
2,31	-1	Exclude		0,000	0,907
Calibration uncertainty	*Calibration_a*	*Calibration_b*	*u(bs_reference)*	*CI Regression*	*CI Calibrated*
1,058	0,907	0,907	0,6700	10,96	11,23

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^3	50		0,975	25 %
	Spring	Summer	Fall	Winter	
Starting month:	3	6	9	12	
DATA SELECTION					
	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*	
CALIBRATION SETTING					
Calibration based on:	SLOPE AND INTERCEPT		**OK**		
RAW DATA			RESULTS AFTER CALIBRATING		
Regression	**1,3y + 6,791**		N (Spring)	0	n
Regression (i=0)	**1,712y**		N (Summer)	48	n
N	48	n	N (Fall)	0	n
			N (Winter)	0	n
Outliers	0	n	Outliers	0	n
Outliers	0,0	%	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
REGRESSION RESULTS (RAW)			REGRESSION RESULTS (CALIBRATED)		
Slope b	**0,7690**	**significant**	**Slope b**	1,1108	
Uncertainty of b	0,0859		Uncertainty of b	0,1117	
Intercept a	**-5,2226**	**significant**	**Intercept a**	-2,7723	
Uncertainty of a	2,3100		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				
EQUIVALENCE TEST (RAW)			EQUIVALENCE 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
STATISTICAL INFORMATION					
Raw data, free intercept					
dxdy	dyy	dxx	rss	uat	u(b)
2739	3192	4647	1727	30	0,086
Raw data, slope forced through origin					
Sxy	Syy	Sxx		u(b)[MaxLike] i=0	u(b_forced)
19589	12634	34716		0,031	0,031
Calibrated, free intercept					
dxdy	dyy	dxx	rss		u(b)
3562	5397	4647	3218		0,112
BACKGROUND AUTOMATION					
Chart descriptions		*Confi.Lvl List*	*Calibration List*	*Stdev of all calibrations in use*	
Description x-axis	RM PM10;Derenda 1	97,5%	Free regression Through origin	0	0,03112
Description y-axis	CM PM10 PNS16D-A	97,5%			
Confi.Lvl	*Calibration Type*	*Filter List*		*Calib. In use (a)*	*Calib. In use (b)*
2,32	-2	Exclude		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

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_2-NO_x, SO_2, CO, O_3) have been accredited according to EN ISO/IEC 17025:2005 since 2009.

Measurement components:

- NO-NO_2-NO_x, SO_2, CO, O_3, PM_{10} & $PM_{2.5}$ with US/EPA heads
  The measurement methods for gas components are those described in the relevant EN-standards i.e. EN14211 for NO-NO_2, EN14212 for SO_2, EN14625 for O_3, EN14626 for CO, and for particulate matter EN12341 and CEN/TS 16450 for PM_{10} and $PM_{2.5}$.

- 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).

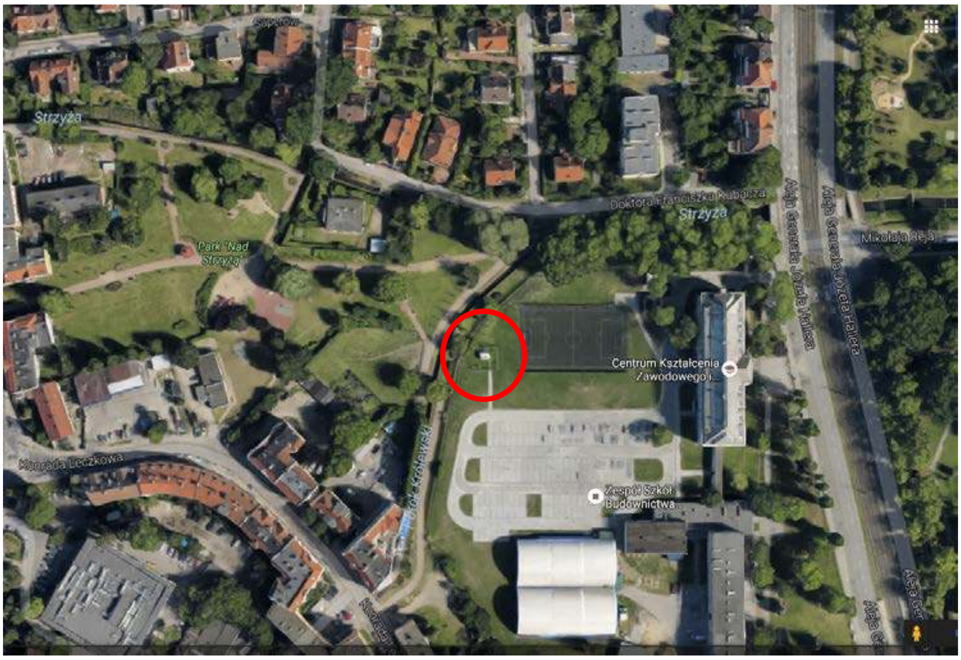
The station is fenced in, locked and secured against interferences. The roof has no railings, but can be accessed with ladder kept at the station.

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).



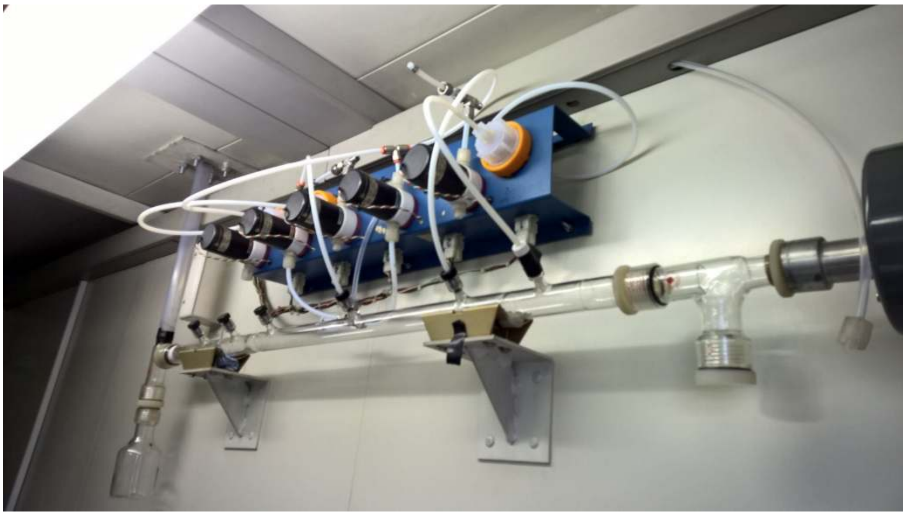
2. Personnel of the station

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

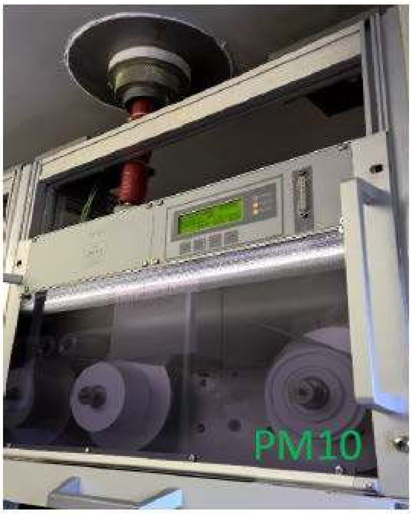
c: Length of the manifold: 1 m above container roof, 1.5 m inside the cabin, not insulated.

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:



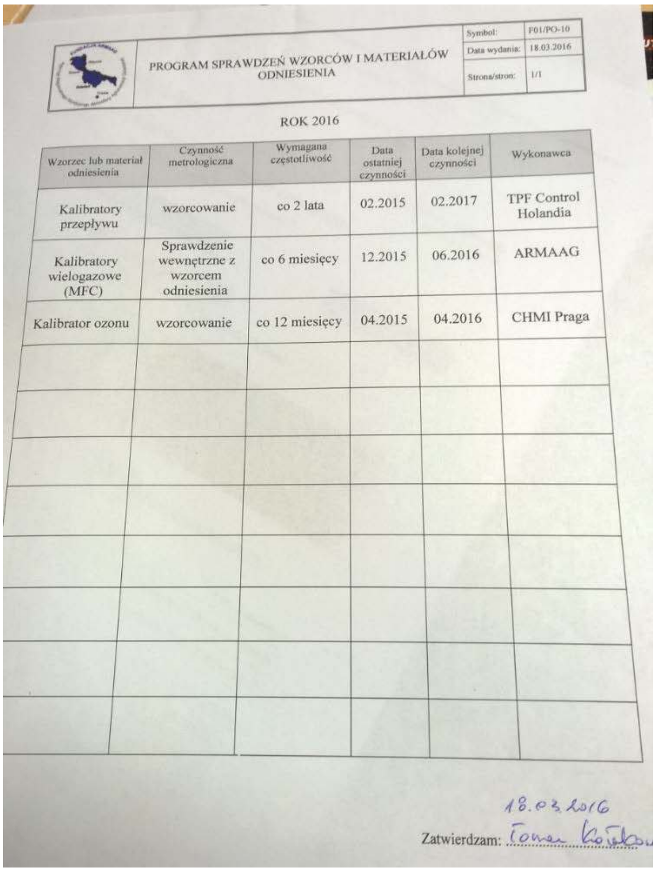
a: Analysers:

- 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 EN-standards i.e. EN14211 for NO-NO_2, EN14212 for SO_2, EN14625 for O_3, EN14626 for CO, and for particulate matter EN12341 for PM_{10} and $PM_{2.5}$.

5. Maintenance and calibrations

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



PROGRAM SPRAWDZEŃ WZORCÓW I MATERIAŁÓW ODNIESIENIA

Symbol: F01/PO-10
Data wydania: 18.03.2016
Strona/stron: 1/1

ROK 2016

Wzorzec lub materiał odniesienia	Czynność metrologiczna	Wymagana częstotliwość	Data ostatniej czynności	Data kolejnej czynności	Wykonawca
Kalibratory przepływu	wzorcowanie	co 2 lata	02.2015	02.2017	TPF Control Holandia
Kalibratory wielogazowe (MFC)	Sprawdzenie wewnętrzne z wzorcem odniesienia	co 6 miesięcy	12.2015	06.2016	ARMAAG
Kalibrator ozonu	wzorcowanie	co 12 miesięcy	04.2015	04.2016	CHMI Praga

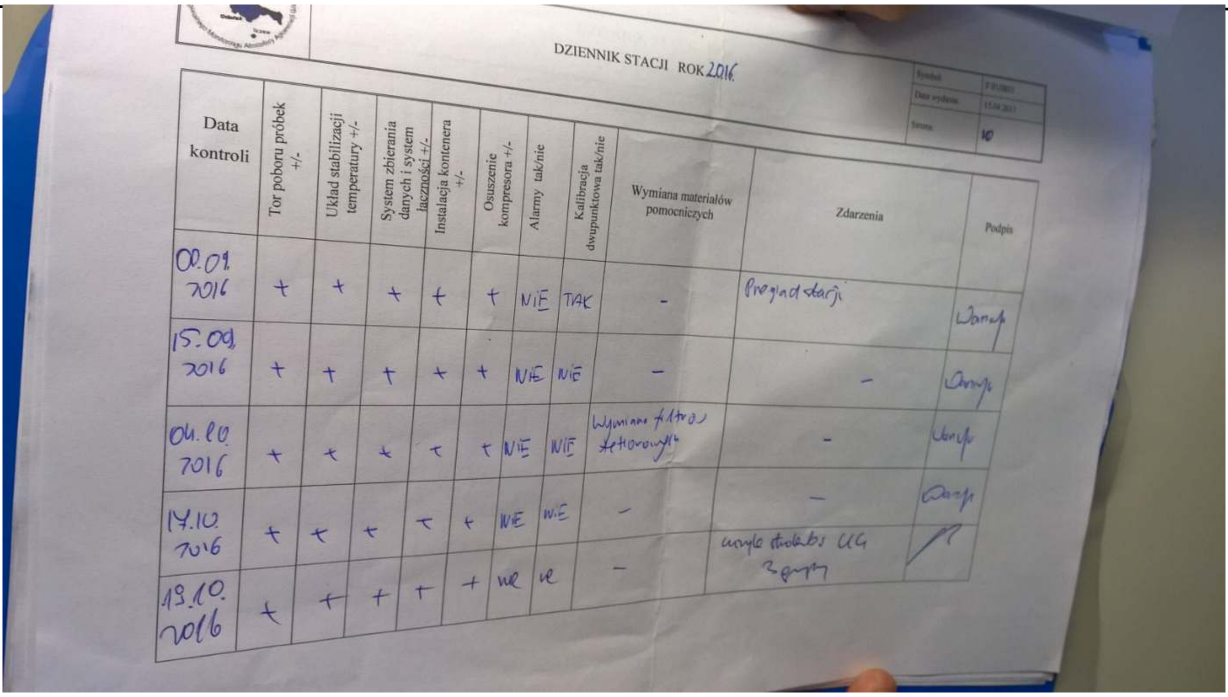
18.03.2016
Zatwierdzam:

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



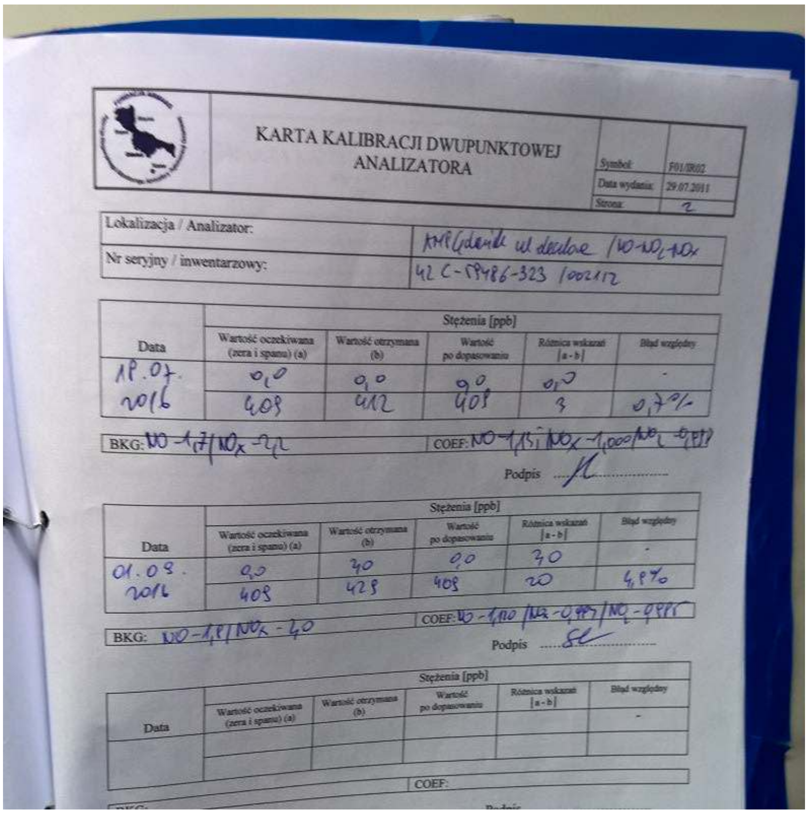
DZIENNIK STACJI ROK 2016

Symbol: [illegible]
Data wydania: [illegible]
Strona: 10

Data kontroli	Tor poboru próbek +/-	Układ stabilizacji temperatury +/-	System zbierania danych i system łączności +/-	Instalacja kontenera +/-	Osuszenie kompresora +/-	Alarmy tak/nie	Kalibracja dwupunktowa tak/nie	Wymiana materiałów pomocniczych	Zdarzenia	Podpis
02.09. 2016	+	+	+	+	+	NIE	TAK	-	Przegląd stacji	
15.09. 2016	+	+	+	+	+	NIE	NIE	-	-	
04.10. 2016	+	+	+	+	+	NIE	NIE	Wymiana filtrów teflonowych	-	
14.10. 2016	+	+	+	+	+	NIE	NIE	-	-	
19.10. 2016	+	+	+	+	+	nie	nie	-	wizyta studentów UG 3 grupy	

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



KARTA KALIBRACJI DWUPUNKTOWEJ ANALIZATORA

Symbol: F01/IR02
Data wydania: 29.07.2011
Strona: 2

Lokalizacja / Analizator: AM1 Gdańsk ul. Leczkowa / NO-NO2-NOx
Nr seryjny / inwentarzowy: 42 C-58486-323 / 002112

Data	Stężenia [ppb]				
	Wartość oczekiwana (zera i spanu) (a)	Wartość otrzymana (b)	Wartość po dopasowaniu	Różnica wskazań |a-b|	Błąd względny
18.07. 2016	0,0	0,0	0,0	0,0	-
	409	412	409	3	0,7%

BKG: NO - 1,7 / NOx - 2,2
COEF: NO - 1,15; NOx - 1,000 / NO2 - 0,999

Podpis ....

Data	Stężenia [ppb]				
	Wartość oczekiwana (zera i spanu) (a)	Wartość otrzymana (b)	Wartość po dopasowaniu	Różnica wskazań |a-b|	Błąd względny
01.08. 2016	0,0	3,0	0,0	3,0	-
	409	429	409	20	4,8%

BKG: NO - 1,8 / NOx - 4,0
COEF: NO - 1,110 / NOx - 0,997 / NO2 - 0,995

Podpis ....

Data	Stężenia [ppb]				
	Wartość oczekiwana (zera i spanu) (a)	Wartość otrzymana (b)	Wartość po dopasowaniu	Różnica wskazań |a-b|	Błąd względny
					-

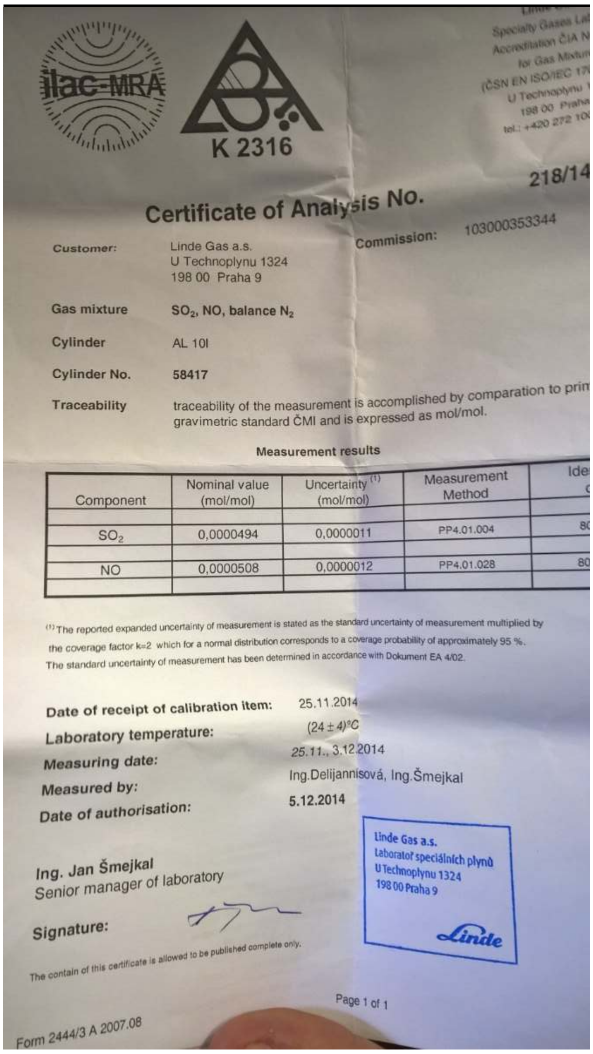
COEF:

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 standard	Cylinder	Certificate nr	Nominal	Analyzed	Exp uncertainty	Date of analysis	Date of expir
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	-



ilac-MRA

K 2316

Specialty Gases La
Accreditation ČIA N
for Gas Mixtur
(ČSN EN ISO/IEC 17
U Technoplynu 1
198 00 Praha
tel.: +420 272 10

Certificate of Analysis No. 218/14

Customer: Linde Gas a.s.
U Technoplynu 1324
198 00 Praha 9

Commission: 103000353344

Gas mixture **SO_2, NO, balance N_2**

Cylinder AL 10l

Cylinder No. **58417**

Traceability traceability of the measurement is accomplished by comparation to prim
gravimetric standard ČMI and is expressed as mol/mol.

Measurement results

Component	Nominal value (mol/mol)	Uncertainty [(1)] (mol/mol)	Measurement Method	Ide
SO_2	0,0000494	0,0000011	PP4.01.004	80
NO	0,0000508	0,0000012	PP4.01.028	80

(1) The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k=2 which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with Dokument EA 4/02.

Date of receipt of calibration item: 25.11.2014
Laboratory temperature: (24 ± 4)°C
Measuring date: 25.11., 3.12.2014
Measured by: Ing.Delijannisová, Ing.Šmejkal
Date of authorisation: 5.12.2014

Ing. Jan Šmejkal
Senior manager of laboratory

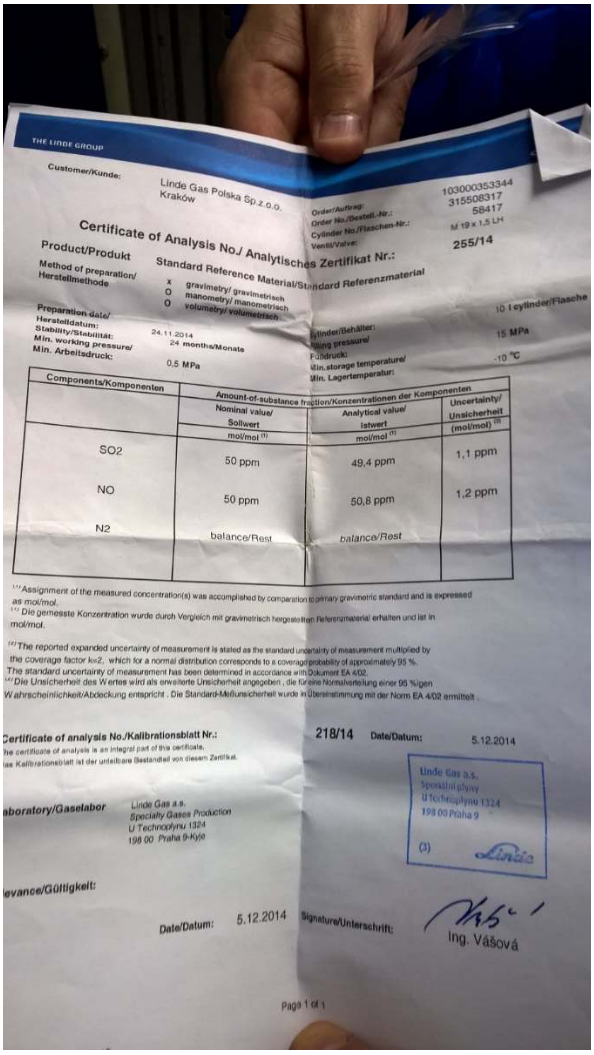
Signature:

Linde Gas a.s.
Laboratoř speciálních plynů
U Technoplynu 1324
198 00 Praha 9
Linde

The contain of this certificate is allowed to be published complete only.

Page 1 of 1

Form 2444/3 A 2007.08



THE LINDE GROUP

Customer/Kunde: Linde Gas Polska Sp.z.o.o.
Kraków

Order/Auftrag: 103000353344
Order No./Bestell.-Nr.: 315508317
Cylinder No./Flaschen-Nr.: 58417
Ventil/Valve: M 19 x 1,5 LH

Certificate of Analysis No./ Analytisches Zertifikat Nr.: 255/14

Product/Produkt Standard Reference Material/Standard Referenzmaterial

Method of preparation/ Herstellmethode
x gravimetry/ gravimetrisch
○ manometry/ manometrisch
○ volumetry/ volumetrisch

Preparation date/ Herstelldatum: 24.11.2014
Stability/Stabilität: 24 months/Monate
Min. working pressure/ Min. Arbeitsdruck: 0,5 MPa

Cylinder/Behälter: 10 l cylinder/Flasche
Filling pressure/ Fülldruck: 15 MPa
Min.storage temperature/ Min. Lagertemperatur: -10 °C

Components/Komponenten	Amount-of-substance fraction/Konzentrationen der Komponenten		
	Nominal value/ Sollwert mol/mol [(1)]	Analytical value/ Istwert mol/mol [(1)]	Uncertainty/ Unsicherheit (mol/mol) [(2)]
SO2	50 ppm	49,4 ppm	1,1 ppm
NO	50 ppm	50,8 ppm	1,2 ppm
N2	balance/Rest	balance/Rest	

(1) Assignment of the measured concentration(s) was accomplished by comparation to primary gravimetric standard and is expressed as mol/mol.
(1) Die gemesste Konzentration wurde durch Vergleich mit gravimetrisch hergestelltem Referenzmaterial erhalten und ist in mol/mol.

(2) The reported expanded uncertainty of measurement is stated as the standard uncertainty of measurement multiplied by the coverage factor k=2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with Dokument EA 4/02.
(2) Die Unsicherheit des Wertes wird als erweiterte Unsicherheit angegeben, die für eine Normalverteilung einer 95 %igen Wahrscheinlichkeit/Abdeckung entspricht. Die Standard-Meßunsicherheit wurde in Übereinstimmung mit der Norm EA 4/02 ermittelt.

ertificate of analysis No./Kalibrationsblatt Nr.: 218/14 **Date/Datum:** 5.12.2014
he certificate of analysis is an integral part of this certificate.
as Kalibrationsblatt ist der unteilbare Bestandteil von diesem Zertifikat.

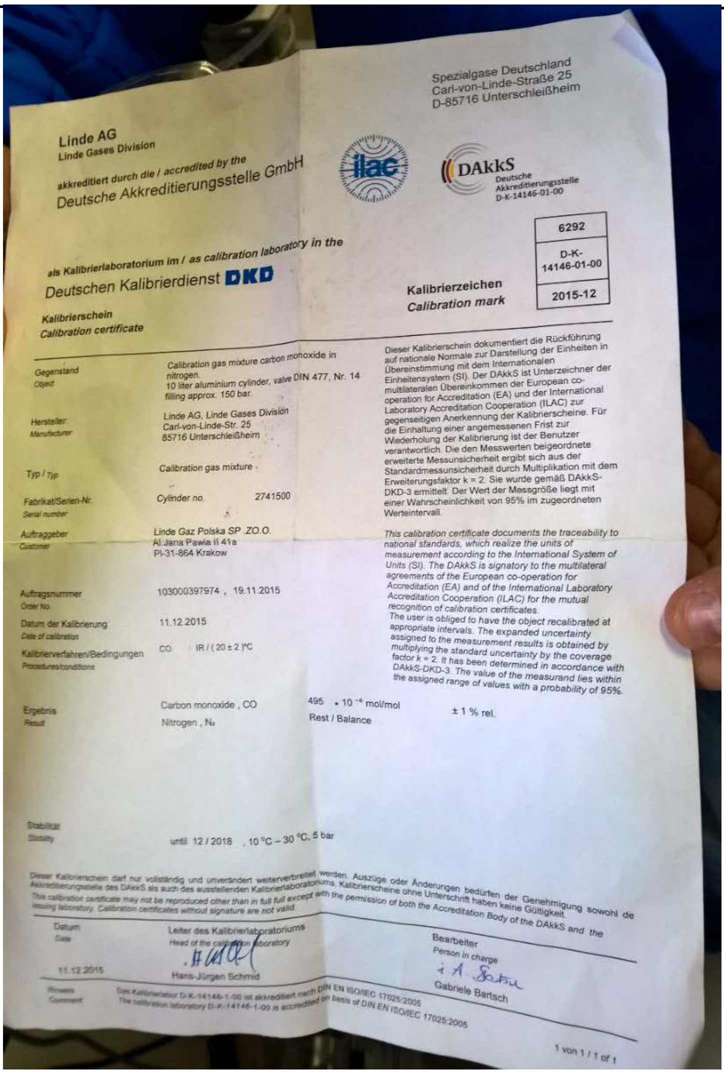
aboratory/Gaselabor Linde Gas a.s.
Specialty Gases Production
U Technoplynu 1324
198 00 Praha 9-Kyje

Linde Gas a.s.
Speciální plyny
U Technoplynu 1324
198 00 Praha 9
(3) Linde

evance/Gültigkeit:

Date/Datum: 5.12.2014 **Signature/Unterschrift:** Ing. Vášová

Page 1 of 1



Spezialgase Deutschland
Carl-von-Linde-Straße 25
D-85716 Unterschleißheim

Linde AG
Linde Gases Division

akkreditiert durch die / accredited by the
Deutsche Akkreditierungsstelle GmbH

DAkkS
Deutsche Akkreditierungsstelle
D-K-14146-01-00

als Kalibrierlaboratorium im / as calibration laboratory in the
Deutschen Kalibrierdienst DKD

Kalibrierschein
Calibration certificate

Kalibrierzeichen *Calibration mark*	6292 D-K-14146-01-00 2015-12

Gegenstand *Object*	Calibration gas mixture carbon monoxide in nitrogen. 10 liter aluminium cylinder, valve DIN 477, Nr. 14 filling approx. 150 bar.
Hersteller *Manufacturer*	Linde AG, Linde Gases Division Carl-von-Linde-Str. 25 85716 Unterschleißheim
Typ / *Typ*	Calibration gas mixture
Fabrikat/Serien-Nr. *Serial number*	Cylinder no. 2741500
Auftraggeber *Customer*	Linde Gaz Polska SP. ZO.O. Al.Jana Pawla II 41a Pl-31-864 Krakow
Auftragsnummer *Order No.*	103000397974 , 19.11.2015
Datum der Kalibrierung *Date of calibration*	11.12.2015
Kalibrierverfahren/Bedingungen *Procedures/conditions*	CO : IR / (20 ± 2)°C

Dieser Kalibrierschein dokumentiert die Rückführung auf nationale Normale zur Darstellung der Einheiten in Übereinstimmung mit dem Internationalen Einheitensystem (SI). Der DAkkS ist Unterzeichner der multilateralen Übereinkommen der European co-operation for Accreditation (EA) und der International Laboratory Accreditation Cooperation (ILAC) zur gegenseitigen Anerkennung der Kalibrierscheine. Für die Einhaltung einer angemessenen Frist zur Wiederholung der Kalibrierung ist der Benutzer verantwortlich. Die den Messwerten beigeordnete erweiterte Messunsicherheit ergibt sich aus der Standardmessunsicherheit durch Multiplikation mit dem Erweiterungsfaktor k = 2. Sie wurde gemäß DAkkS-DKD-3 ermittelt. Der Wert der Messgröße liegt mit einer Wahrscheinlichkeit von 95% im zugeordneten Werteintervall.

This calibration certificate documents the traceability to national standards, which realize the units of measurement according to the International System of Units (SI). The DAkkS is signatory to the multilateral agreements of the European co-operation for Accreditation (EA) and of the International Laboratory Accreditation Cooperation (ILAC) for the mutual recognition of calibration certificates. The user is obliged to have the object recalibrated at appropriate intervals. The expanded uncertainty assigned to the measurement results is obtained by multiplying the standard uncertainty by the coverage factor k = 2. It has been determined in accordance with DAkkS-DKD-3. The value of the measurand lies within the assigned range of values with a probability of 95%.

Ergebnis *Result*	Carbon monoxide , CO	495 · 10^{-6} mol/mol	± 1 % rel.
	Nitrogen , N_2	Rest / Balance	

Stabilität
Stability until 12 / 2018 , 10 °C – 30 °C, 5 bar

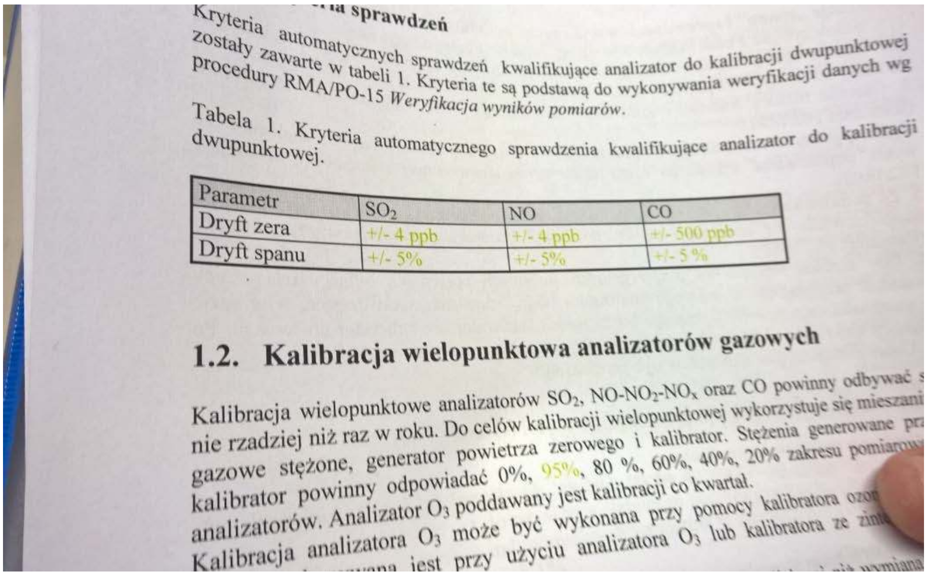
Dieser Kalibrierschein darf nur vollständig und unverändert weiterverbreitet werden. Auszüge oder Änderungen bedürfen der Genehmigung sowohl de[illegible] Akkreditierungsstelle des DAkkS als auch des ausstellenden Kalibrierlaboratoriums. Kalibrierscheine ohne Unterschrift haben keine Gültigkeit.
This calibration certificate may not be reproduced other than in full full except with the permission of both the Accreditation Body of the DAkkS and the issuing laboratory. Calibration certificates without signature are not valid.

Datum *Date*	Leiter des Kalibrierlaboratoriums *Head of the calibration laboratory*	Bearbeiter *Person in charge*
11.12.2015	Hans-Jürgen Schmid	Gabriele Bartsch

Hinweis
Comment
Das Kalibrierlabor D-K-14146-1-00 ist akkreditiert nach DIN EN ISO/IEC 17025:2005
The calibration laboratory D-K-14146-1-00 is accredited on basis of DIN EN ISO/IEC 17025:2005

1 von 1 / 1 of 1

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



ia sprawdzeń

Kryteria automatycznych sprawdzeń kwalifikujące analizator do kalibracji dwupunktowej zostały zawarte w tabeli 1. Kryteria te są podstawą do wykonywania weryfikacji danych wg procedury RMA/PO-15 *Weryfikacja wyników pomiarów*.

Tabela 1. Kryteria automatycznego sprawdzenia kwalifikujące analizator do kalibracji dwupunktowej.

Parametr	SO_2	NO	CO
Dryft zera	+/- 4 ppb	+/- 4 ppb	+/- 500 ppb
Dryft spanu	+/- 5%	+/- 5%	+/- 5 %

1.2. Kalibracja wielopunktowa analizatorów gazowych

Kalibracja wielopunktowe analizatorów SO_2, NO-NO_2-NO_x oraz CO powinny odbywać
nie rzadziej niż raz w roku. Do celów kalibracji wielopunktowej wykorzystuje się mieszani
gazowe stężone, generator powietrza zerowego i kalibrator. Stężenia generowane pr
kalibrator powinny odpowiadać 0%, 95%, 80 %, 60%, 40%, 20% zakresu pomiarow
analizatorów. Analizator O_3 poddawany jest kalibracji co kwartał.
Kalibracja analizatora O_3 może być wykonana przy pomocy kalibratora ozo
wana jest przy użyciu analizatora O_3 lub kalibratora ze zint

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.

l: 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. *FprEN 16450 standard: 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. *FprEN 16450 standard: 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.

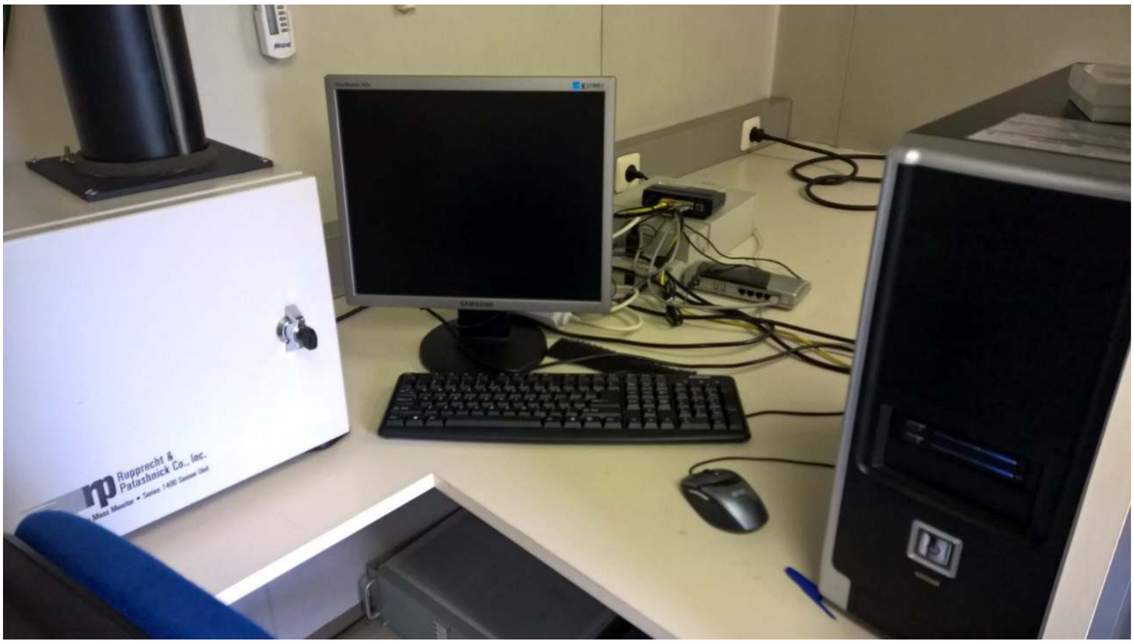
8. Data collection

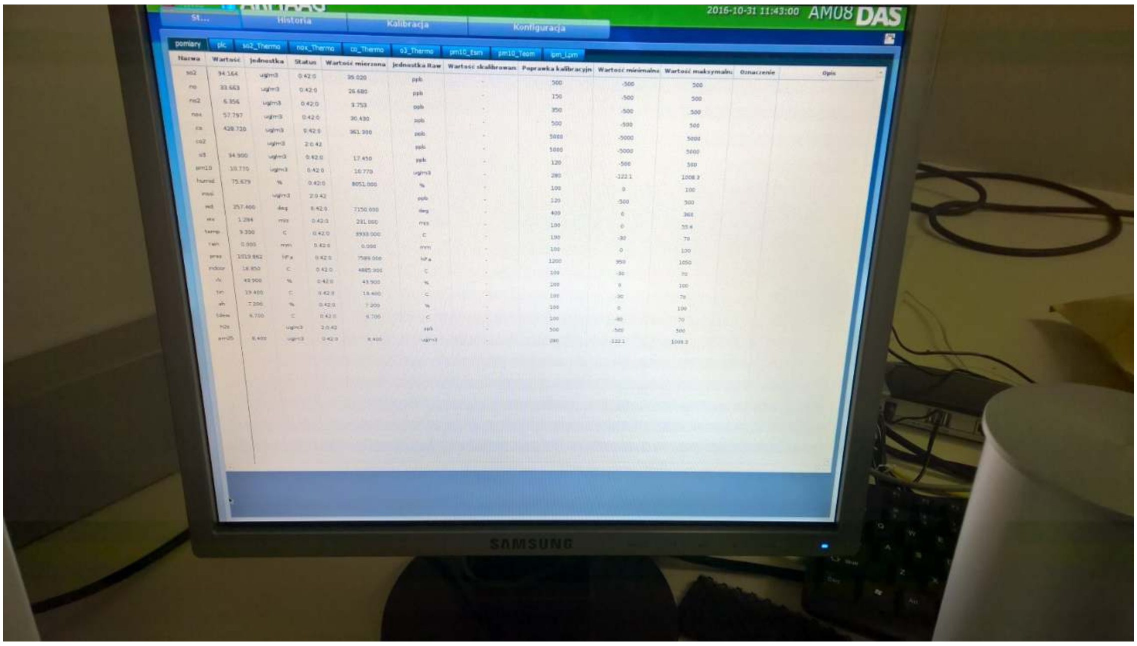
a: Data acquisition system: ENVIRO

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.

e: Complains (4.8) Treatment of complains is stated in the Quality manual and a separate SOP. There is a register for complaints (not assessed).

f: 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).

h: Internal audits (4.14) Internal audits are performed annually including documentation and activities at the site. In addition, an annual management review is organized.

i: 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)

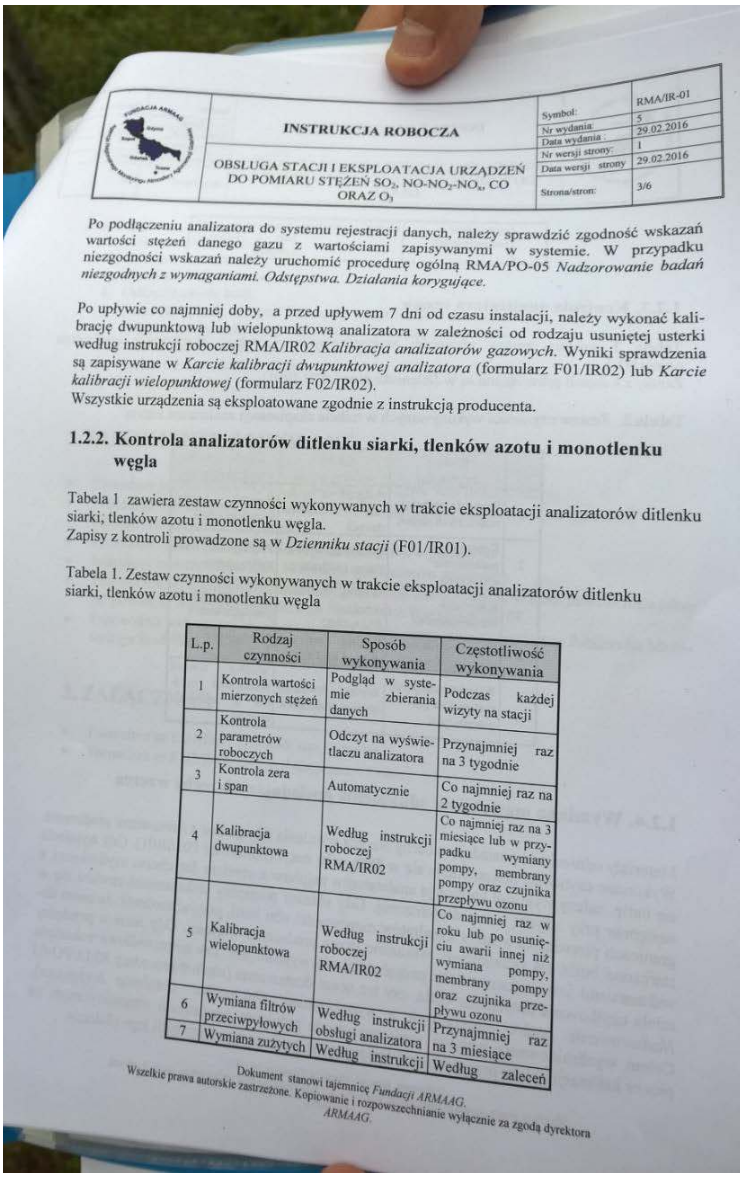
1. Supervision and management of procedures (document control)
2. Co-operation with customers
3. Supervision of complaints
4. Delivery and service (purchasing services and supplies)
5. Control of nonconforming testing work
6. Improvements

7. Internal audits
8. Training
9. 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)

<u>Technical instructions</u>

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.)



	INSTRUKCJA ROBOCZA	Symbol:	RMA/IR-01
		Nr wydania:	5
		Data wydania :	29.02.2016
	OBSŁUGA STACJI I EKSPLOATACJA URZĄDZEŃ DO POMIARU STĘŻEŃ SO_2, $NO-NO_2-NO_x$, CO ORAZ O_3	Nr wersji strony:	1
		Data wersji strony	29.02.2016
		Strona/stron:	3/6

Po podłączeniu analizatora do systemu rejestracji danych, należy sprawdzić zgodność wskazań wartości stężeń danego gazu z wartościami zapisywanymi w systemie. W przypadku niezgodności wskazań należy uruchomić procedurę ogólną RMA/PO-05 *Nadzorowanie badań niezgodnych z wymaganiami. Odstępstwa. Działania korygujące.*

Po upływie co najmniej doby, a przed upływem 7 dni od czasu instalacji, należy wykonać kalibrację dwupunktową lub wielopunktową analizatora w zależności od rodzaju usuniętej usterki według instrukcji roboczej RMA/IR02 *Kalibracja analizatorów gazowych*. Wyniki sprawdzenia są zapisywane w *Karcie kalibracji dwupunktowej analizatora* (formularz F01/IR02) lub *Karcie kalibracji wielopunktowej* (formularz F02/IR02).
Wszystkie urządzenia są eksploatowane zgodnie z instrukcją producenta.

1.2.2. Kontrola analizatorów ditlenku siarki, tlenków azotu i monotlenku węgla

Tabela 1 zawiera zestaw czynności wykonywanych w trakcie eksploatacji analizatorów ditlenku siarki; tlenków azotu i monotlenku węgla.
Zapisy z kontroli prowadzone są w *Dzienniku stacji* (F01/IR01).

Tabela 1. Zestaw czynności wykonywanych w trakcie eksploatacji analizatorów ditlenku siarki, tlenków azotu i monotlenku węgla

L.p.	Rodzaj czynności	Sposób wykonywania	Częstotliwość wykonywania
1	Kontrola wartości mierzonych stężeń	Podgląd w systemie zbierania danych	Podczas każdej wizyty na stacji
2	Kontrola parametrów roboczych	Odczyt na wyświetlaczu analizatora	Przynajmniej raz na 3 tygodnie
3	Kontrola zera i span	Automatycznie	Co najmniej raz na 2 tygodnie
4	Kalibracja dwupunktowa	Według instrukcji roboczej RMA/IR02	Co najmniej raz na 3 miesiące lub w przypadku wymiany pompy, membrany pompy oraz czujnika przepływu ozonu
5	Kalibracja wielopunktowa	Według instrukcji roboczej RMA/IR02	Co najmniej raz w roku lub po usunięciu awarii innej niż wymiana pompy, membrany pompy oraz czujnika przepływu ozonu
6	Wymiana filtrów przeciwpyłowych	Według instrukcji obsługi analizatora	Przynajmniej raz na 3 miesiące
7	Wymiana zużytych	Według instrukcji	Według zaleceń

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: ≤ -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.

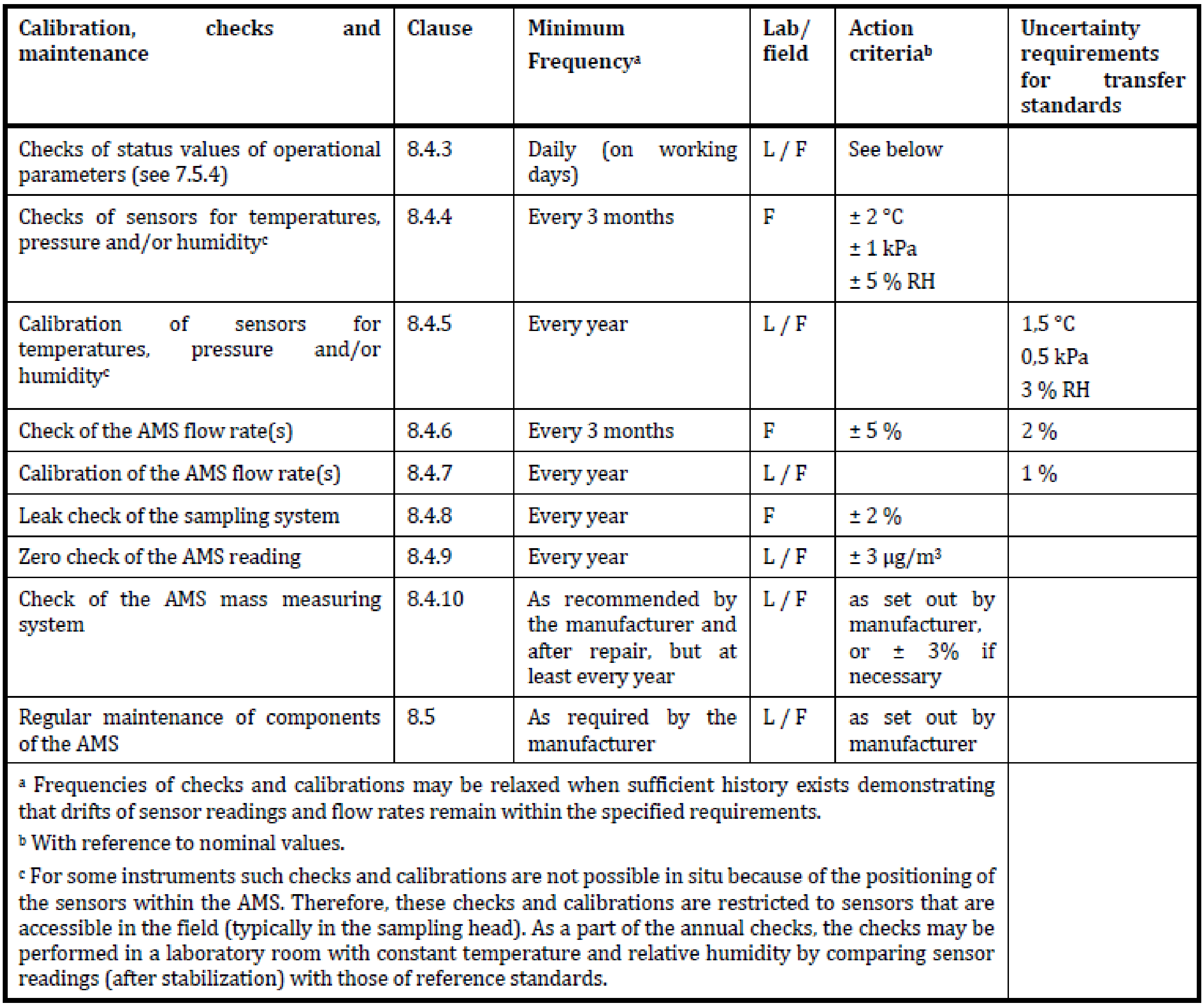
c The particulate filter shall be changed periodically depending on the dust loading at the sampling site. During this filter change the filter housing shall be cleaned. Overloading of the particulate filter may change the concentration of nitrogen monoxide and/or nitrogen dioxide.

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[a]	Lab / field	Action criteria[b]	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[c]	8.4.4	Every 3 months	F	± 2 °C ± 1 kPa ± 5 % RH	
Calibration of sensors for temperatures, pressure and/or humidity[c]	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	

[a] 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.

[c] 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.

ILMATIETEEN LAITOS
METEOROLOGISKA INSTITUTET
FINNISH METEOROLOGICAL INSTITUTE

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

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_Sj9CPykssy0xPLMnMz0vMAfIjo8ziAwy9Ai2cDB0N_N0t3Qw8Q7wD3Py8ffydnQz1wwkpiAJKG-AAjgb6BbmhigDFKUNa/dz/d5/L2dBISEvZ0FBIS9nQSEh/)

Measurement components, Femman:

- NO_x, SO_2, O_3, PM_{10} & $PM_{2.5}$ with US/EPA heads
  The measurement methods for gas components are those described in the relevant EN-standards i.e. EN14211 for NO-NO_2, EN14212 for SO_2, EN14625 for O_3, and for particulate matter EN12341. CEN/TS 16450 for PM_{10} and $PM_{2.5}$ 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_x, PM_{10} with US/EPA heads
  The measurement methods for gas components are those described in the relevant EN-standards i.e. EN14211 for NO-NO_2 and EN12341 for PM_{10}.

- 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.

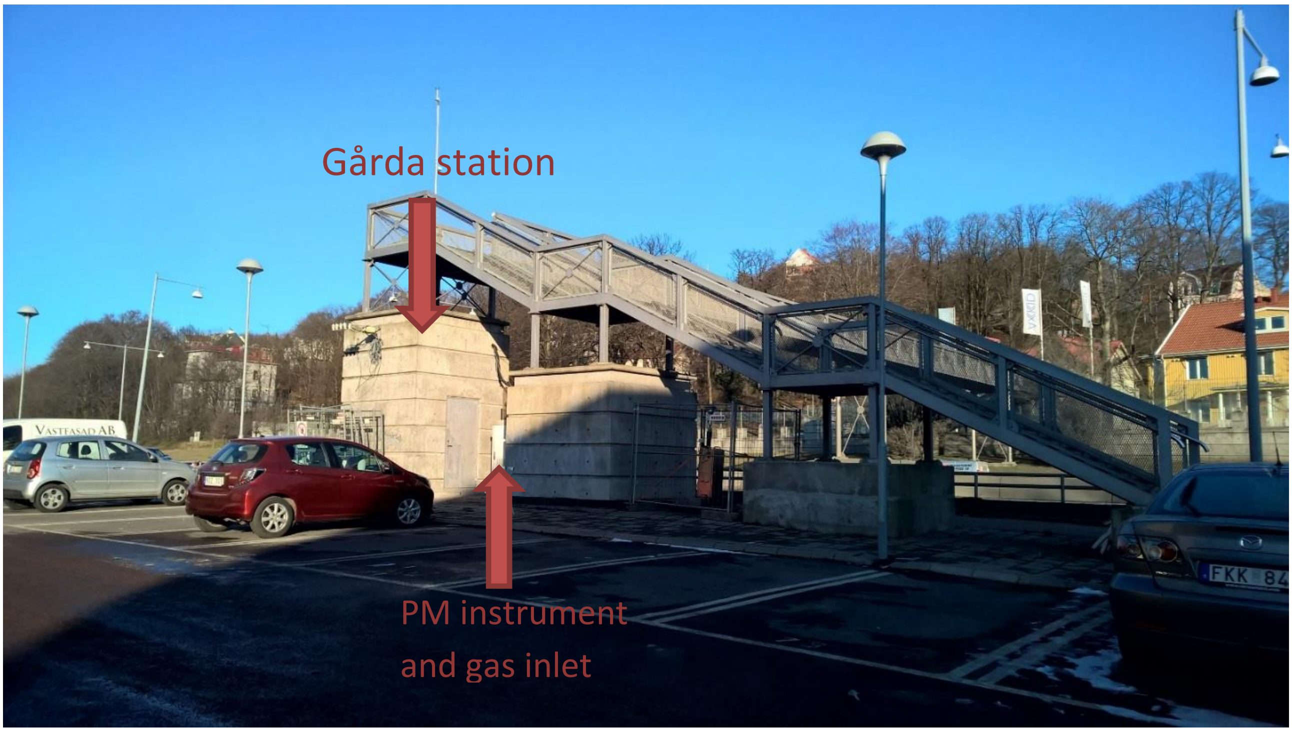
b: Description of the station:

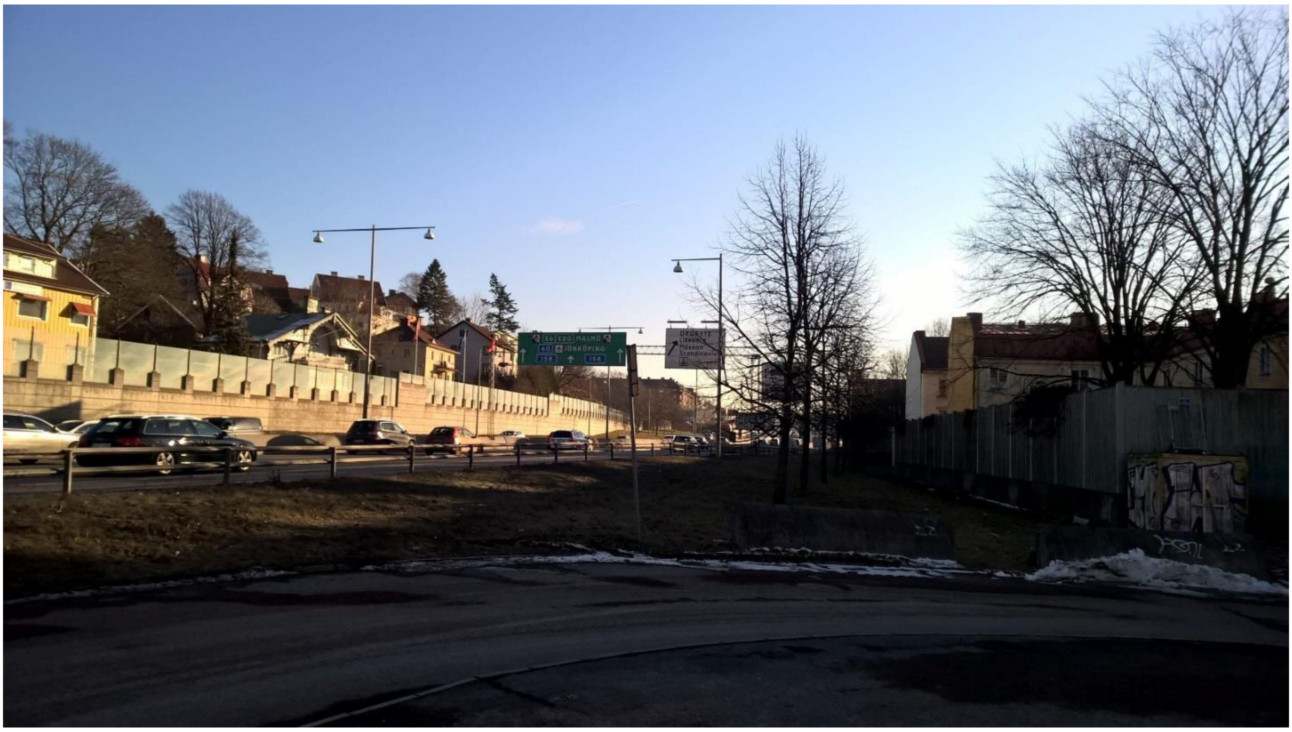
Femman is located in the centre of Gothenburg on the rooftop of a shopping mall Nordstan. The measurements are performed at a height of about 30 m. The building is surrounded by roads. The station facilities are located in the top floor (7th) of the mall with access to the mall roof by ladders where 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.

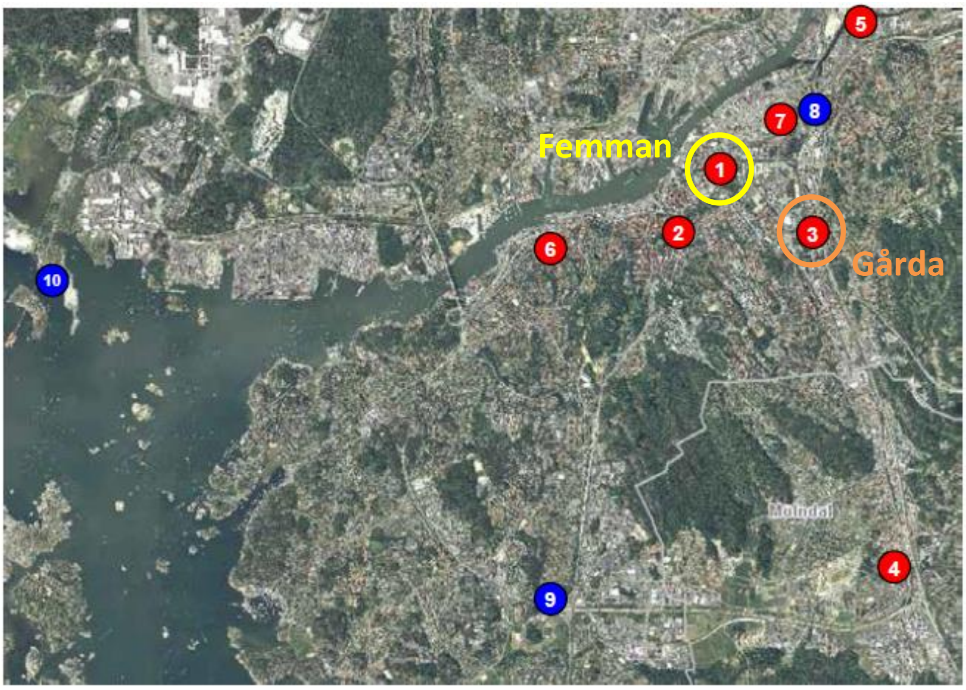
Photo of and around Gårda:





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.

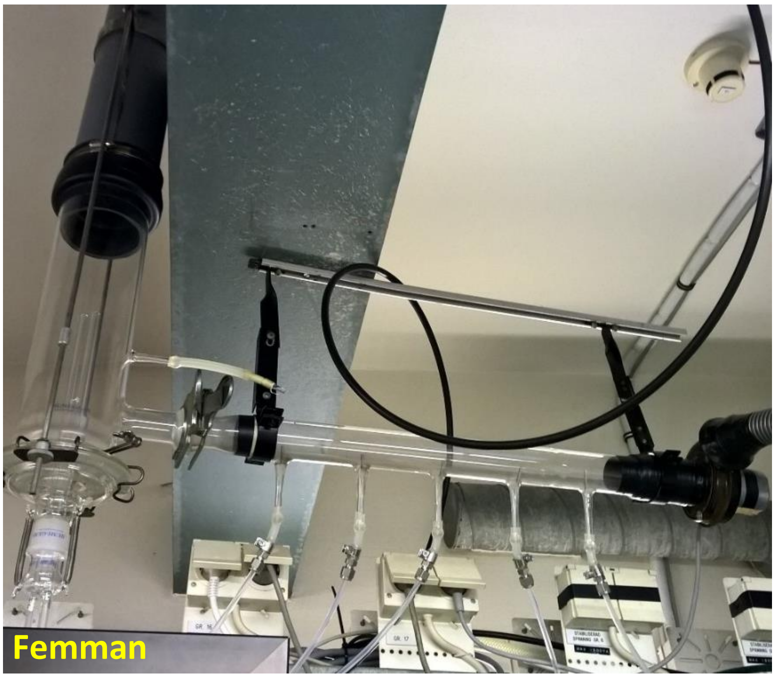
Emma Björkman: NOx measurements, calibrations, measurement uncertainties, written air quality reports, responsible person for Gårda and deputy for Femman.

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.

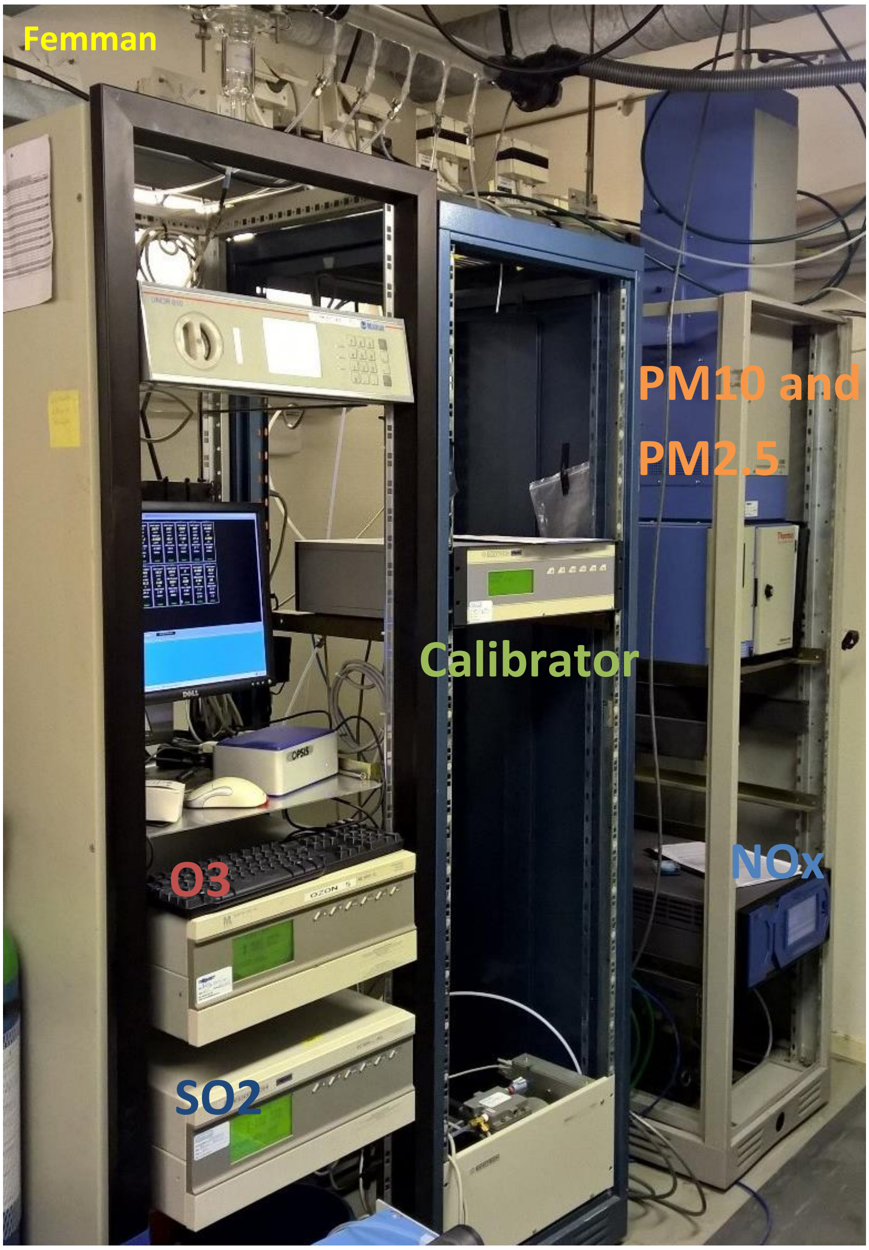
d: Flow rate inside the manifold: Not known. Pump is attached to the end of the manifold.

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 EN-standards i.e. EN14211 for NO-NO_2, EN14212 for SO_2, EN14625 for O_3, and EN12341 for PM_{10} and $PM_{2.5}$.

Station Gårda

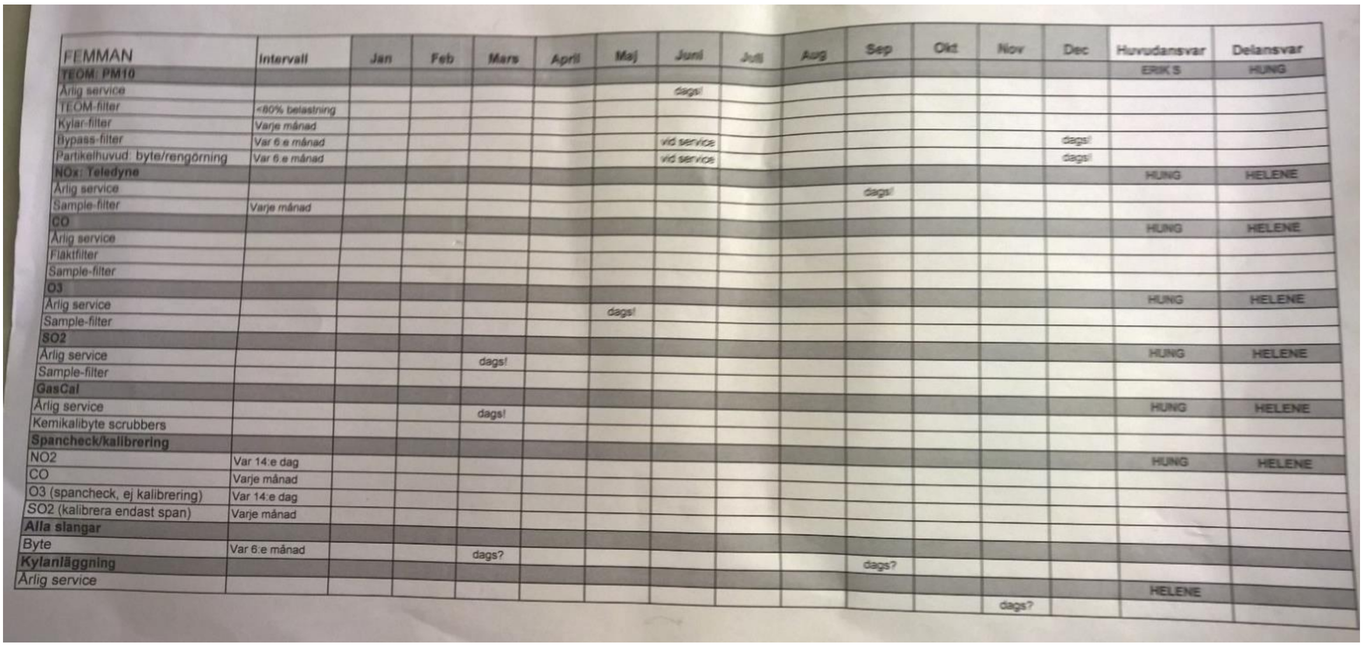
- NOx, Thermo Scientific 42i
- PM10, TEOM 1400 AB with US/EPA head
- No gas calibrator at the site. The NOx monitor is calibrated with a gas cylinder tested at Femman before use.

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).

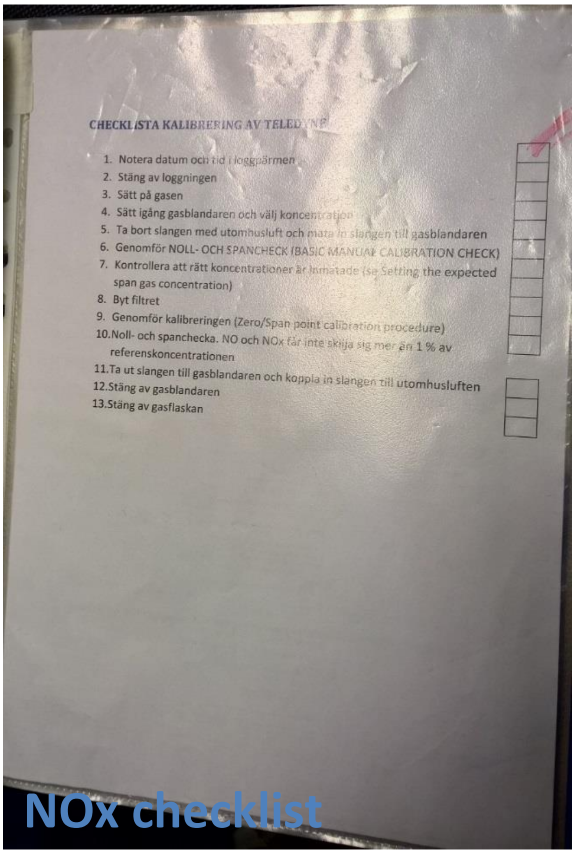


FEMMAN	Intervall	Jan	Feb	Mars	April	Maj	Juni	Juli	Aug	Sep	Okt	Nov	Dec	Huvudansvar	Delansvar
TEOM: PM10														ERIK S	HUNG
Årlig service							dags!								
TEOM-filter	<80% belastning														
Kylar-filter	Varje månad														
Bypass-filter	Var 6:e månad						vid service						dags!		
Partikelhuvud: byte/rengörning	Var 6:e månad						vid service						dags!		
NOx: Teledyne														HUNG	HELENE
Årlig service										dags!					
Sample-filter	Varje månad														
CO														HUNG	HELENE
Årlig service															
Fläktfilter															
Sample-filter															
O3														HUNG	HELENE
Årlig service						dags!									
Sample-filter															
SO2														HUNG	HELENE
Årlig service				dags!											
Sample-filter															
GasCal														HUNG	HELENE
Årlig service				dags!											
Kemikalibyte scrubbers															
Spancheck/kalibrering														HUNG	HELENE
NO2	Var 14:e dag														
CO	Varje månad														
O3 (spancheck, ej kalibrering)	Var 14:e dag														
SO2 (kalibrera endast span)	Varje månad														
Alla slangar															
Byte	Var 6:e månad			dags?						dags?					
Kylanläggning														HELENE	
Årlig service												dags?			

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.

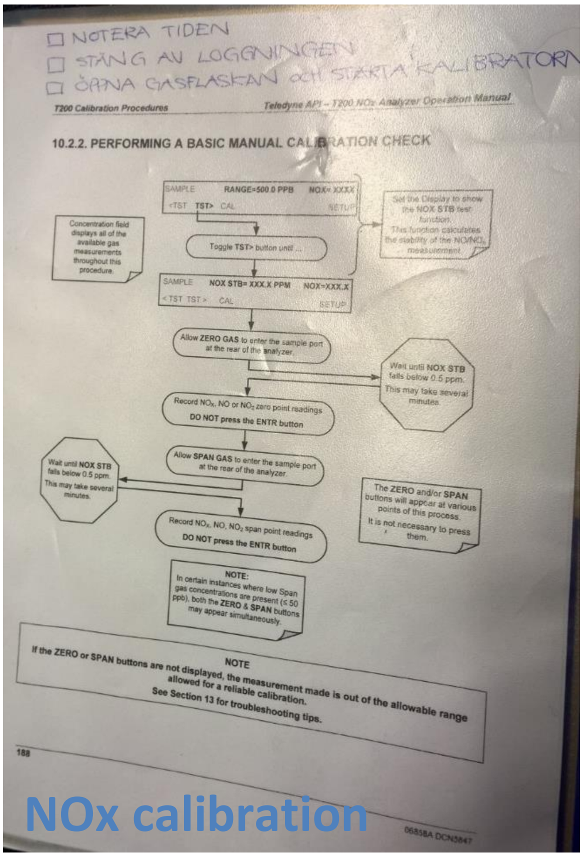
d: Actions during the maintenance: Check for instrument operation and alarm lights, zero and span checks, filter changes for gas and PM monitors, TEOM check and leak test, change on PM inlets, change of consumables when needed.



CHECKLISTA KALIBRERING AV TELEDYNE

1. Notera datum och tid i loggpärmen ☐
2. Stäng av loggningen ☐
3. Sätt på gasen ☐
4. Sätt igång gasblandaren och välj koncentration ☐
5. Ta bort slangen med utomhusluft och mata in slangen till gasblandaren ☐
6. Genomför NOLL- OCH SPANCHECK (BASIC MANUAL CALIBRATION CHECK) ☐
7. Kontrollera att rätt koncentrationer är inmatade (se Setting the expected span gas concentration) ☐
8. Byt filtret ☐
9. Genomför kalibreringen (Zero/Span point calibration procedure) ☐
10. Noll- och spanchecka. NO och NOx får inte skilja sig mer än 1 % av referenskoncentrationen ☐
11. Ta ut slangen till gasblandaren och koppla in slangen till utomhusluften ☐
12. Stäng av gasblandaren ☐
13. Stäng av gasflaskan ☐

NOx checklist



☐ NOTERA TIDEN
☐ STÄNG AV LOGGNINGEN
☐ ÖPPNA GASFLASKAN OCH STARTA KALIBRATORN

T200 Calibration Procedures — Teledyne API – T200 NOx Analyzer Operation Manual

10.2.2. PERFORMING A BASIC MANUAL CALIBRATION CHECK

SAMPLE RANGE=500.0 PPB NOX= XXXX
<TST TST> CAL SETUP

Concentration field displays all of the available gas measurements throughout this procedure.

Set the Display to show the NOX STB test function.
This function calculates the stability of the NO/NO$_2$ measurement

Toggle TST> button until ...

SAMPLE NOX STB= XXX.X PPM NOX=XXX.X
<TST TST> CAL SETUP

Allow ZERO GAS to enter the sample port at the rear of the analyzer.

Wait until NOX STB falls below 0.5 ppm.
This may take several minutes.

Record NO$_X$, NO or NO$_2$ zero point readings
DO NOT press the ENTR button

Allow SPAN GAS to enter the sample port at the rear of the analyzer.

Wait until NOX STB falls below 0.5 ppm.
This may take several minutes.

The ZERO and/or SPAN buttons will appear at various points of this process.
It is not necessary to press them.

Record NO$_X$, NO, NO$_2$ span point readings
DO NOT press the ENTR button

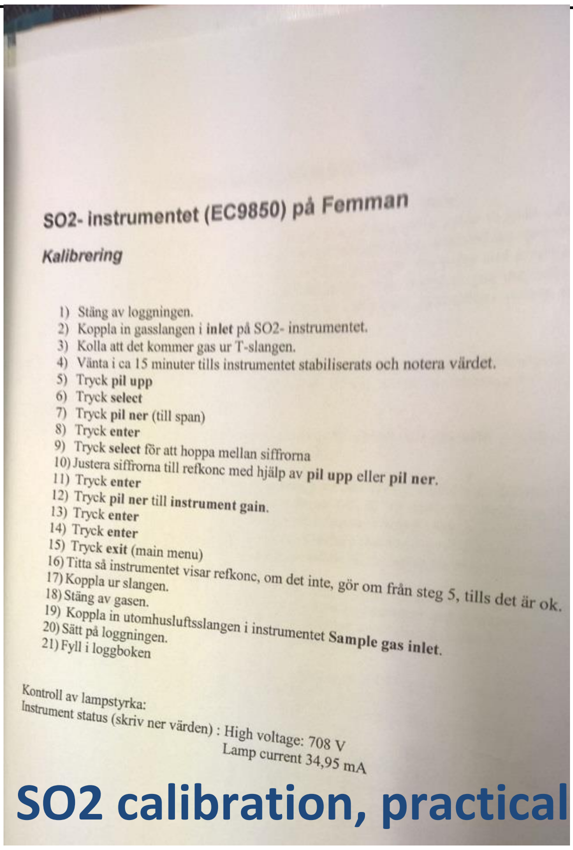
NOTE:
In certain instances where low Span gas concentrations are present (≤ 50 ppb), both the ZERO & SPAN buttons may appear simultaneously.

NOTE
If the ZERO or SPAN buttons are not displayed, the measurement made is out of the allowable range allowed for a reliable calibration.
See Section 13 for troubleshooting tips.

188

06858A DCN5847

NOx calibration



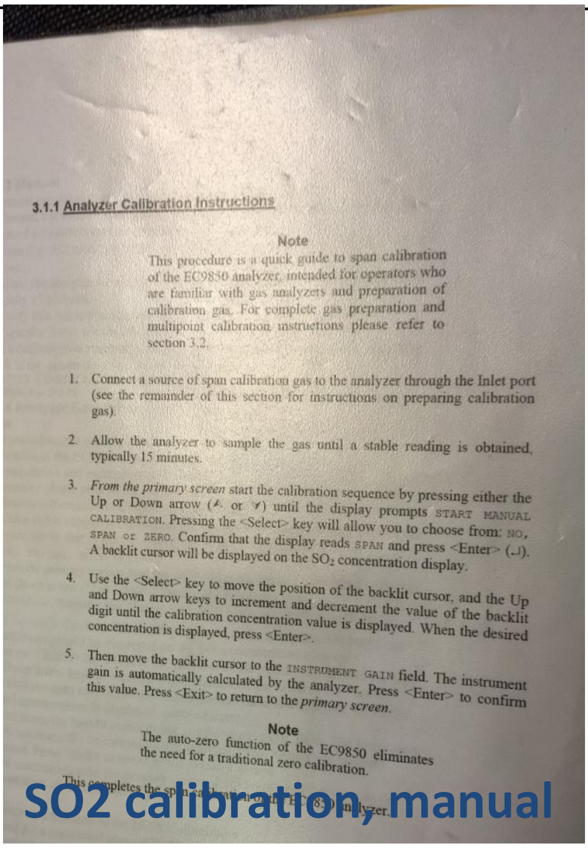
SO2- instrumentet (EC9850) på Femman

Kalibrering

1) Stäng av loggningen.
2) Koppla in gasslangen i **inlet** på SO2- instrumentet.
3) Kolla att det kommer gas ur T-slangen.
4) Vänta i ca 15 minuter tills instrumentet stabiliserats och notera värdet.
5) 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 siffrorna till refkonc med hjälp av **pil upp** eller **pil ner.**
11) Tryck **enter**
12) Tryck **pil ner** till **instrument gain.**
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) Stäng av gasen.
19) Koppla in utomhusluftsslangen i instrumentet **Sample gas inlet.**
20) Sätt på loggningen.
21) Fyll i loggboken

Kontroll av lampstyrka:
Instrument status (skriv ner värden) : High voltage: 708 V
Lamp current 34,95 mA

SO2 calibration, practical



3.1.1 Analyzer Calibration Instructions

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 instructions please refer to section 3.2.

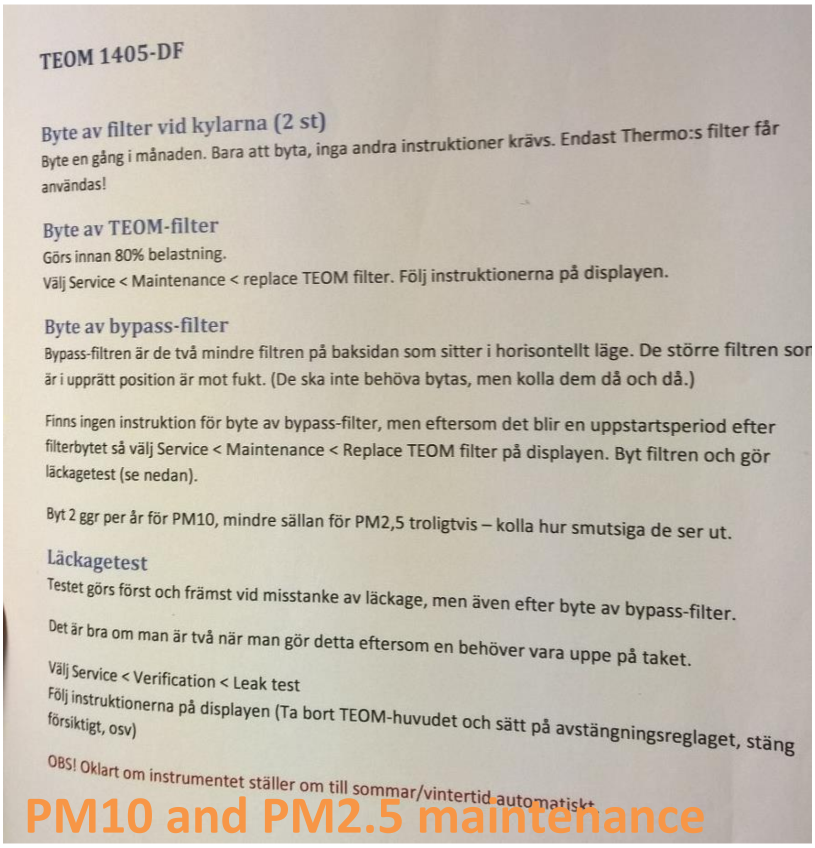
1. Connect a source of span calibration gas to the analyzer through the Inlet port (see the remainder of this section for instructions on preparing calibration gas).
2. Allow the analyzer to sample the gas until a stable reading is obtained, typically 15 minutes.
3. *From the primary screen* start the 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: `NO`, `SPAN or ZERO`. Confirm that the display reads `SPAN` and press <Enter> (↵). A backlit cursor will be displayed on the SO_2 concentration display.
4. 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>.
5. 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.

This completes the span calibration of the EC9850 analyzer.

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.

Läckagetest

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 försiktigt, osv)

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

PM10 and PM2.5 maintenance

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.

EN standards: 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 standard	Cylinder	Certificate nr	Nominal (ppm)	Analyzed (ppm)	Exp uncertainty	Date of analysis	Date of 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: ≥ 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 (≤ -4 or ≥ 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.

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: 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.

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

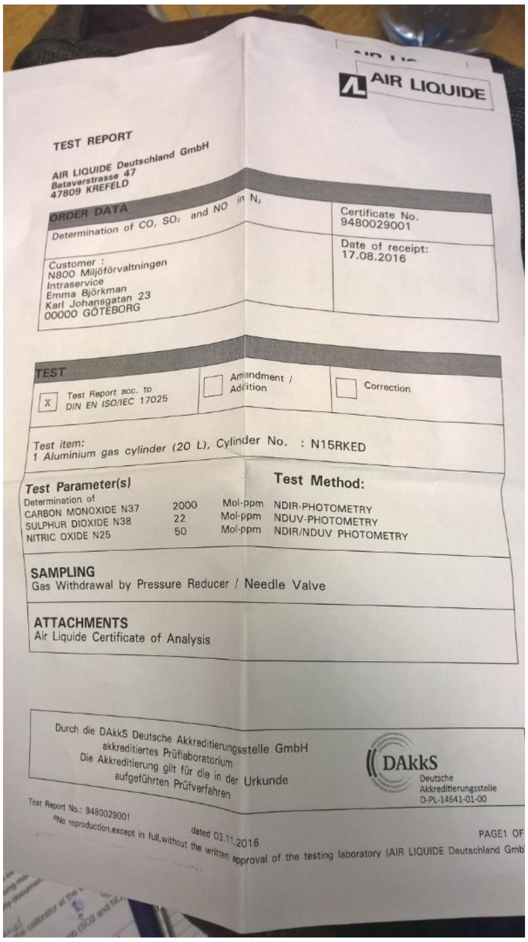
m: Traceability of calibration standards (ISO 17025; 5.6) :

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.



AIR LIQUIDE

TEST REPORT

AIR LIQUIDE Deutschland GmbH
Bataverstrasse 47
47809 KREFELD

ORDER DATA	
Determination of CO, SO₂ and NO in N₂	Certificate No. 9480029001
Customer : N800 Miljöförvaltningen Intraservice Emma Björkman Karl Johansgatan 23 00000 GÖTEBORG	Date of receipt: 17.08.2016

TEST

☒ Test Report acc. to DIN EN ISO/IEC 17025 ☐ Amendment / Addition ☐ Correction

Test item:
1 Aluminium gas cylinder (20 L), Cylinder No. : N15RKED

Test Parameter(s) Determination of			Test Method:
CARBON MONOXIDE N37	2000	Mol-ppm	NDIR-PHOTOMETRY
SULPHUR DIOXIDE N38	22	Mol-ppm	NDUV-PHOTOMETRY
NITRIC OXIDE N25	50	Mol-ppm	NDIR/NDUV PHOTOMETRY

SAMPLING
Gas Withdrawal by Pressure Reducer / Needle Valve

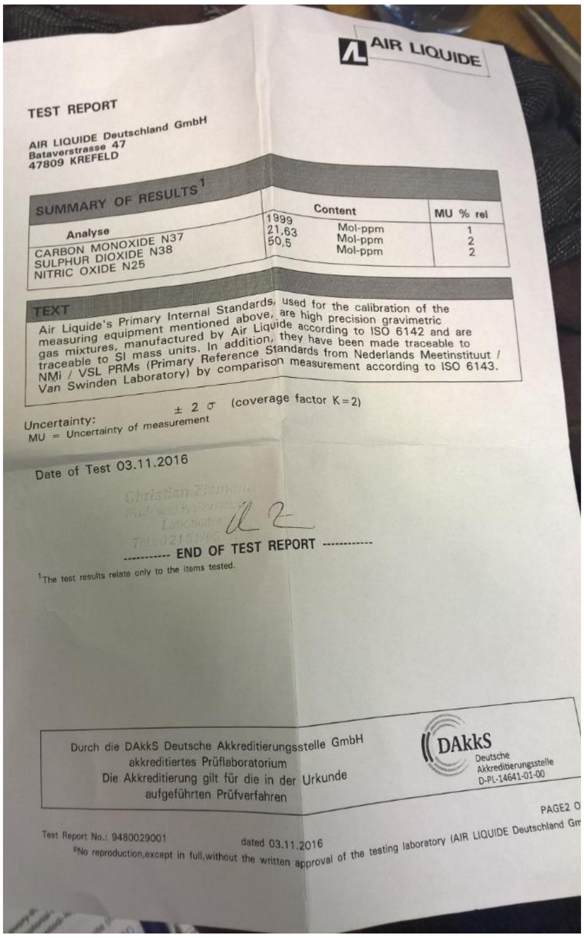
ATTACHMENTS
Air Liquide Certificate of Analysis

Durch die DAkkS Deutsche Akkreditierungsstelle GmbH
akkreditiertes Prüflaboratorium
Die Akkreditierung gilt für die in der Urkunde
aufgeführten Prüfverfahren

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-14641-01-00

Test Report No.: 9480029001 dated 03.11.2016 PAGE1 OF

©No reproduction,except in full,without the written approval of the testing laboratory (AIR LIQUIDE Deutschland Gmb



AIR LIQUIDE

TEST REPORT

AIR LIQUIDE Deutschland GmbH
Bataverstrasse 47
47809 KREFELD

SUMMARY OF RESULTS[1]

Analyse	Content		MU % rel
CARBON MONOXIDE N37	1999	Mol-ppm	1
SULPHUR DIOXIDE N38	21,63	Mol-ppm	2
NITRIC OXIDE N25	50,5	Mol-ppm	2

TEXT

Air Liquide's Primary Internal Standards, used for the calibration of the measuring equipment mentioned above, are high precision gravimetric gas mixtures, manufactured by Air Liquide according to ISO 6142 and are traceable to SI mass units. In addition, they have been made traceable to NMi / VSL PRMs (Primary Reference Standards from Nederlands Meetinstituut / Van Swinden Laboratory) by comparison measurement according to ISO 6143.

Uncertainty: ± 2 σ (coverage factor K=2)
MU = Uncertainty of measurement

Date of Test 03.11.2016

---------- END OF TEST REPORT ----------

[1] The test results relate only to the items tested.

Durch die DAkkS Deutsche Akkreditierungsstelle GmbH
akkreditiertes Prüflaboratorium
Die Akkreditierung gilt für die in der Urkunde
aufgeführten Prüfverfahren

DAkkS
Deutsche
Akkreditierungsstelle
D-PL-14641-01-00

Test Report No.: 9480029001 dated 03.11.2016 PAGE2 O

©No reproduction,except in full,without the written approval of the testing laboratory (AIR LIQUIDE Deutschland Gm

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.

  FprEN 16450 standard: 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.

  FprEN 16450 standard: 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.

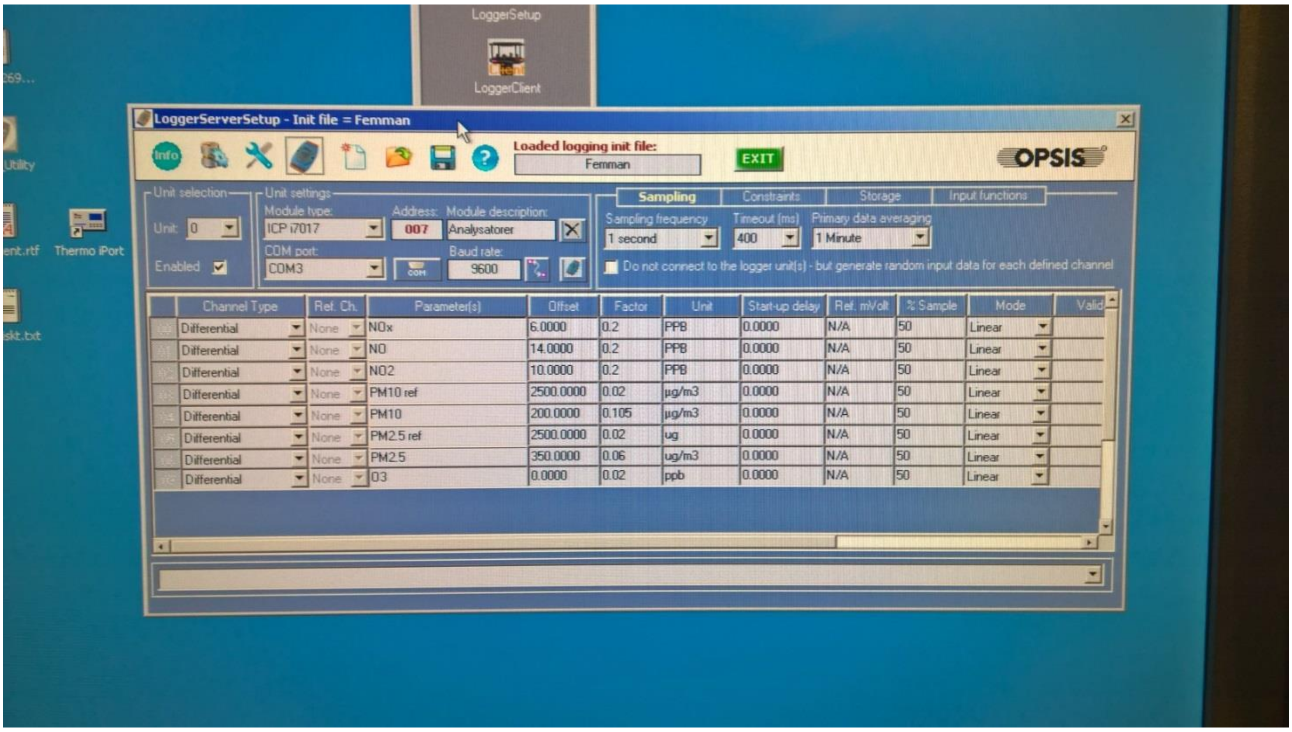
c: Do you crease the impactor plate of the inlet: Since the network is using US-EPA inlets, greasing is not needed.

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 http://www.aces.su.se/reflab/wp-content/uploads/2016/11/ACES_Report_4.pdf.

8. Data collection

a: Data acquisition system: EnviMan



LoggerServerSetup - Init file = Femman

Loaded logging init file: Femman

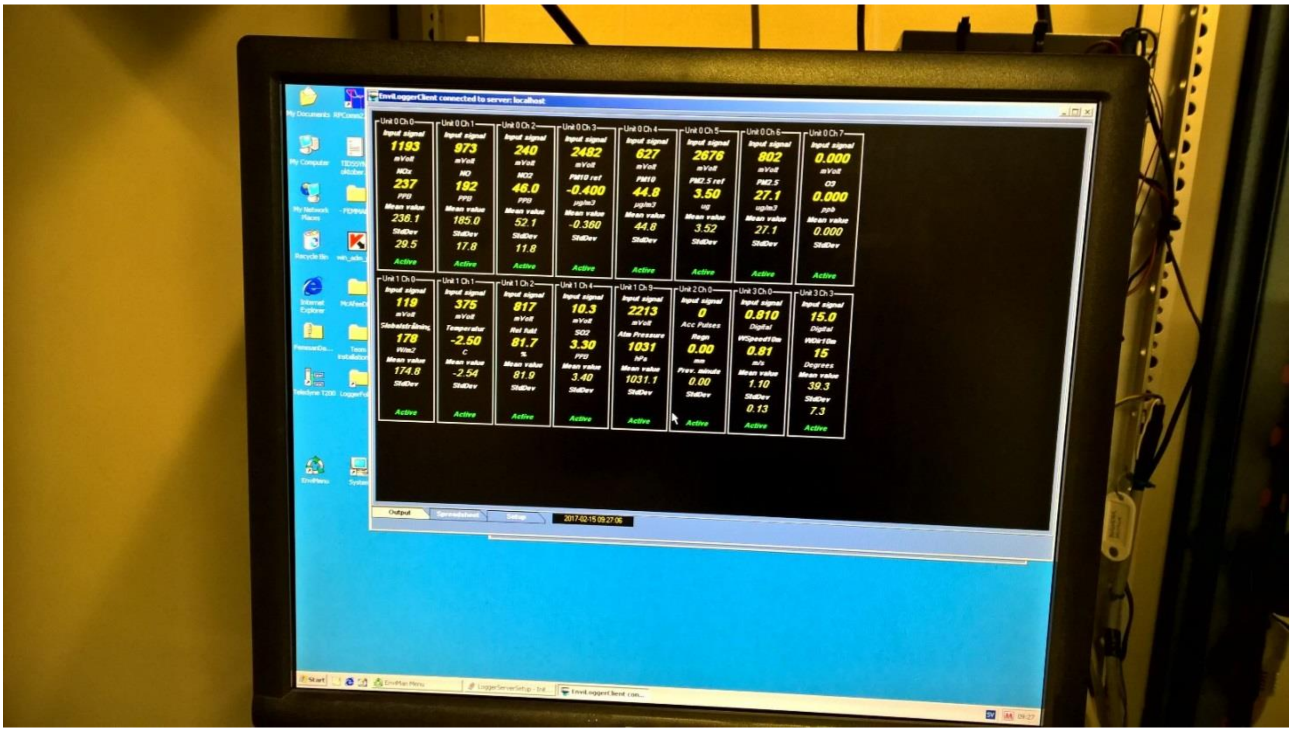
Unit selection
Unit: 0
Enabled ☑

Unit settings
Module type: ICP i7017
Address: 007
Module description: Analysatorer
COM port: COM3
Baud rate: 9600

Sampling frequency: 1 second
Timeout (ms): 400
Primary data averaging: 1 Minute

☐ Do not connect to the logger unit(s) - but generate random input data for each defined channel

Channel Type	Ref. Ch.	Parameter(s)	Offset	Factor	Unit	Start-up delay	Ref. mVolt	% Sample	Mode	Valid
Differential	None	NOx	6.0000	0.2	PPB	0.0000	N/A	50	Linear	
Differential	None	NO	14.0000	0.2	PPB	0.0000	N/A	50	Linear	
Differential	None	NO2	10.0000	0.2	PPB	0.0000	N/A	50	Linear	
Differential	None	PM10 ref	2500.0000	0.02	µg/m3	0.0000	N/A	50	Linear	
Differential	None	PM10	200.0000	0.105	µg/m3	0.0000	N/A	50	Linear	
Differential	None	PM2.5 ref	2500.0000	0.02	ug	0.0000	N/A	50	Linear	
Differential	None	PM2.5	350.0000	0.06	ug/m3	0.0000	N/A	50	Linear	
Differential	None	O3	0.0000	0.02	ppb	0.0000	N/A	50	Linear	

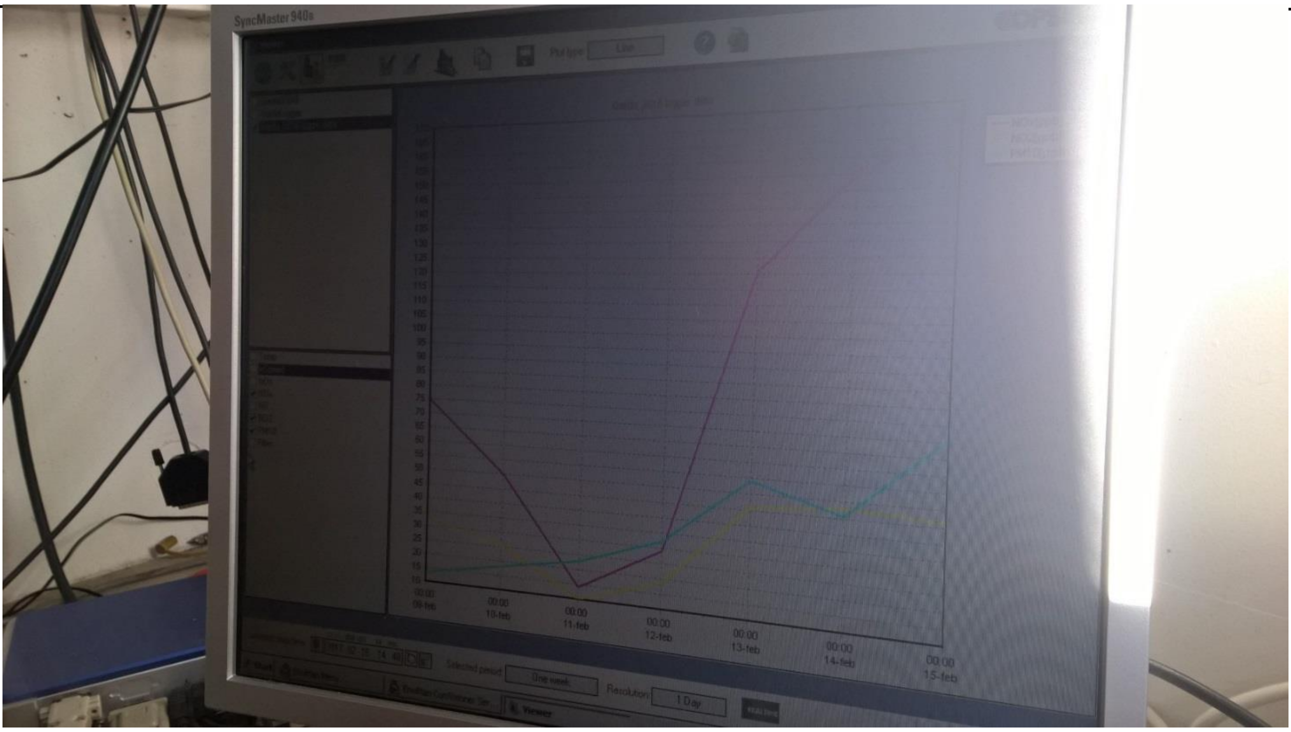


EnviLoggerClient connected to server: localhost

Unit 0 Ch 0	Unit 0 Ch 1	Unit 0 Ch 2	Unit 0 Ch 3	Unit 0 Ch 4	Unit 0 Ch 5	Unit 0 Ch 6	Unit 0 Ch 7
Input signal	Input signal	Input signal	Input signal	Input signal	Input signal	Input signal	Input signal
1193	973	240	2482	627	2676	802	0.000
mVolt	mVolt	mVolt	mVolt	mVolt	mVolt	mVolt	mVolt
NOx	NO	NO2	PM10 ref	PM10	PM2.5 ref	PM2.5	O3
237	192	46.0	-0.400	44.8	3.50	27.1	0.000
PPB	PPB	PPB	µg/m3	µg/m3	ug	ug/m3	ppb
Mean value	Mean value	Mean value	Mean value	Mean value	Mean value	Mean value	Mean value
236.1	185.0	52.1	-0.360	44.8	3.52	27.1	0.000
StdDev	StdDev	StdDev	StdDev	StdDev	StdDev	StdDev	StdDev
29.5	17.8	11.8					
Active	Active	Active	Active	Active	Active	Active	Active

Unit 1 Ch 0	Unit 1 Ch 1	Unit 1 Ch 2	Unit 1 Ch 4	Unit 1 Ch 9	Unit 2 Ch 0	Unit 3 Ch 0	Unit 3 Ch 3
Input signal	Input signal	Input signal	Input signal	Input signal	Input signal	Input signal	Input signal
119	375	817	10.3	2213	0	0.810	15.0
mVolt	mVolt	mVolt	mVolt	mVolt	Acc Pulses	Digital	Digital
Globalstrålning	Temperatur	Rel fukt	SO2	Atm Pressure	Regn	WSpeed10m	WDir10m
178	-2.50	81.7	3.30	1031	0.00	0.81	15
W/m2	C	%	PPB	hPa	mm	m/s	Degrees
Mean value	Mean value	Mean value	Mean value	Mean value	Prev. minute	Mean value	Mean value
174.8	-2.54	81.9	3.40	1031.1	0.00	1.10	39.3
StdDev	StdDev	StdDev	StdDev	StdDev	StdDev	StdDev	StdDev
						0.13	7.3
Active	Active	Active	Active	Active	Active	Active	Active

2017-02-15 09:27:06



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.

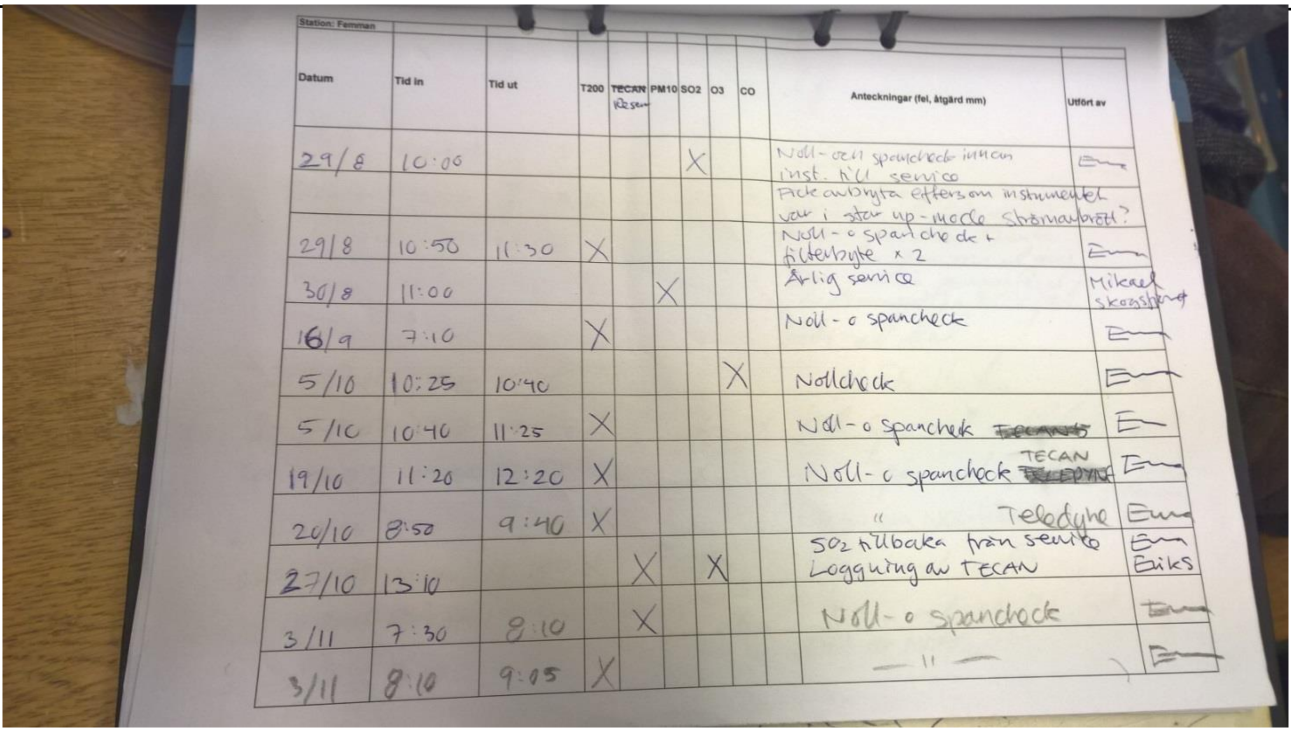
e: Is there any QA/QC procedures for data validation and reporting?

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.



Station: Femman

Datum	Tid in	Tid ut	T200	~~TECAN~~ Reserv	PM10	SO2	O3	CO	Anteckningar (fel, åtgärd mm)	Utfört av
29/8	10:00					X			Noll- och spancheck innan inst. till service	
									Icke avbryta eftersom instrumentet var i star up-mode Strömavbrott?	
29/8	10:50	11:30	X						Noll- o spancheck + filterbyte x 2	
30/8	11:00				X				Årlig service	Mikael Skogsberg
16/9	7:10		X						Noll- o spancheck	
5/10	10:25	10:40					X		Nollcheck	
5/10	10:40	11:25	X						Noll- o spancheck ~~TECAN~~	
19/10	11:20	12:20	X						Noll- o spancheck TECAN ~~TELEDYNE~~	
20/10	8:50	9:40	X						" Teledyne	
27/10	13:10			X		X			SO2 tillbaka från service Loggning av TECAN	Eriks
3/11	7:30	8:10		X					Noll- o spancheck	
3/11	8:10	9:05	X						— " —	

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.

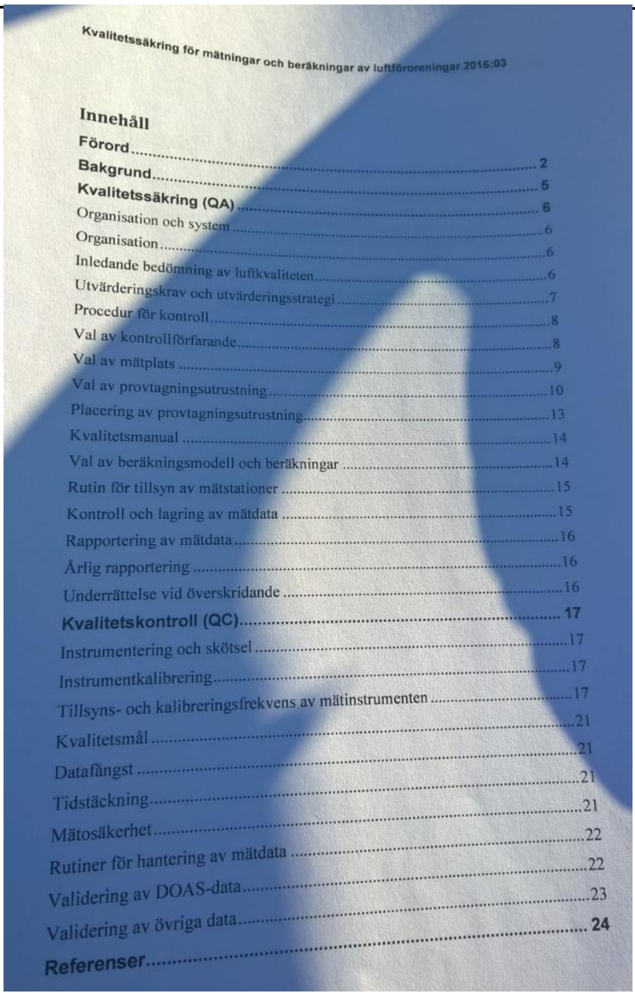
10. Audits

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).



Kvalitetssäkring för mätningar och beräkningar av luftföroreningar 2016:03

Innehåll

Förord 2
Bakgrund 5
Kvalitetssäkring (QA) 6
Organisation och system 6
Organisation 6
Inledande bedömning av luftkvaliteten 6
Utvärderingskrav och utvärderingsstrategi 7
Procedur för kontroll 8
Val av kontrollförfarande 8
Val av mätplats 9
Val av provtagningsutrustning 10
Placering av provtagningsutrustning 13
Kvalitetsmanual 14
Val av beräkningsmodell och beräkningar 14
Rutin för tillsyn av mätstationer 15
Kontroll och lagring av mätdata 15
Rapportering av mätdata 16
Årlig rapportering 16
Underrättelse vid överskridande 16
Kvalitetskontroll (QC) 17
Instrumentering och skötsel 17
Instrumentkalibrering 17
Tillsyns- och kalibreringsfrekvens av mätinstrumenten 17
Kvalitetsmål 21
Datafångst 21
Tidstäckning 21
Mätosäkerhet 21
Rutiner för hantering av mätdata 22
Validering av DOAS-data 22
Validering av övriga data 23
Referenser 24

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.

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

f: Improvements (4.9) Not applicable.

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

h: 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.

i: 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

Katriina Kyllönen, 20.3.2017

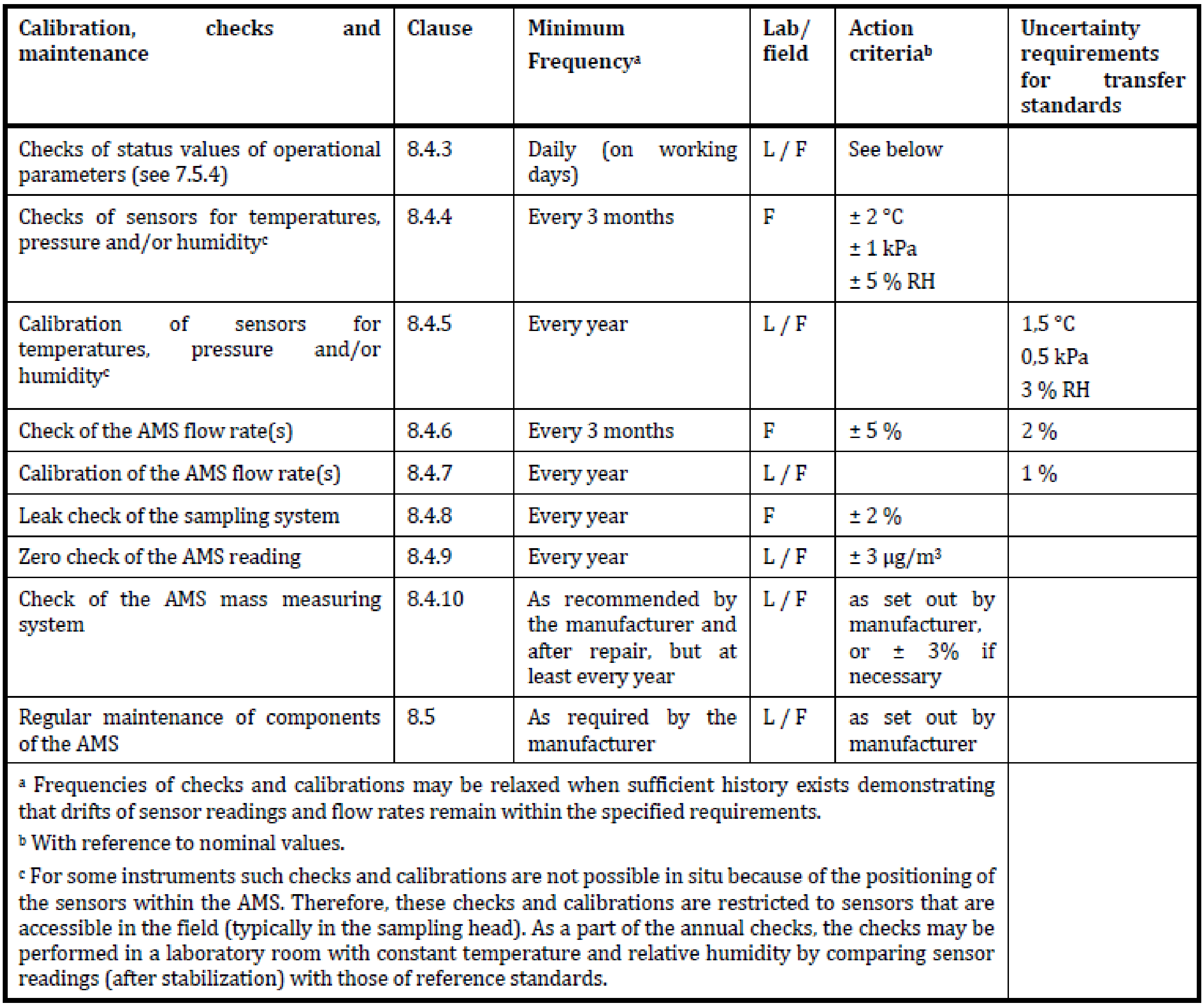
Table 1. The checks and calibrations together with their frequency; gas measurements

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[a]	Lab/ field	Action criteria[b]	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[c]	8.4.4	Every 3 months	F	± 2 °C ± 1 kPa ± 5 % RH	
Calibration of sensors for temperatures, pressure and/or humidity[c]	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	

[a] 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.

[c] 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:

Kaisa Lusa
Jari Walden
Finnish Meteorological Institute
Research and Development/Air Quality Research
P.O. 503 FI-00100 Helsinki Finland
kaisa.lusa@fmi.fi, jari.walden@fmi.fi
P. +358 50 3269426 (Kaisa Lusa)
P. +358 50 5914615 (Jari Walden)
Fax: +358 9 19295403

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_2-NO_x, SO_2, CO, O_3) have been accredited according to EN ISO/IEC 17025:2005 since 2006.

Measurement components:

- NO-NO_2-NO_x, SO_2, CO, O_3, PM_{10} & $PM_{2.5}$
- 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_x: Thermo 42C
- CO: CO 12M Environnement s.A
- O_3: Horiba APOA-370
- $PM_{2,5}$: Derenda
- Zero gas: Filtered air and zero air generator.

See photos below:

b: Analysers in the laboratory:

- NO_x: AC32M Environnement s.A
- SO_2: AF22M Environnement s.A, Thermo 43C, Horiba APSA-370 (2 pcs)
- CO: CO 12M Environnement s.A (3 pcs), Thermo 48C (2 pcs)
- O_3: O_3 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:

1. 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_2). 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/m^3
- SO_2: about 180-250 µg/m^3
- CO: about 1,0 – 1,5 mg/m^3

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:

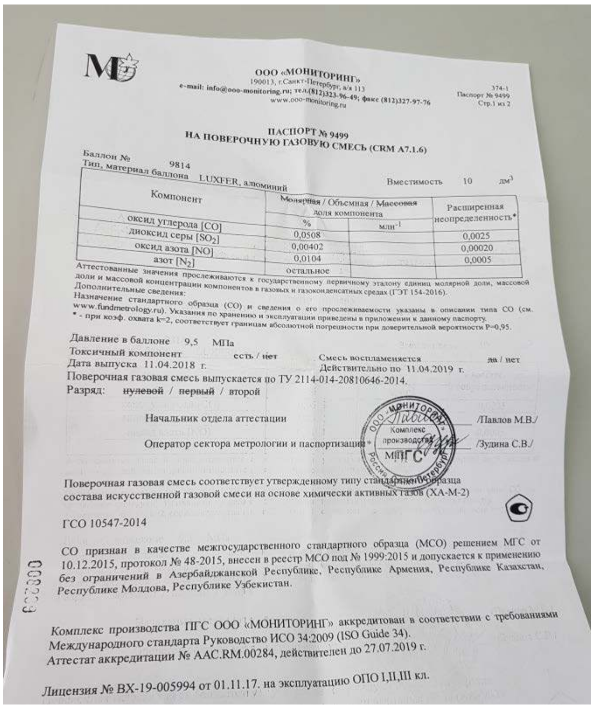
Linearity is checked annually and also if there has been made some maintenance for the analyzer.

l: 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.



ООО «МОНИТОРИНГ»
190013, г.Санкт-Петербург, а/я 113
e-mail: info@ooo-monitoring.ru; тел.(812)323-96-49; факс (812)327-97-76
www.ooo-monitoring.ru

374-1
Паспорт № 9499
Стр.1 из 2

ПАСПОРТ № 9499
НА ПОВЕРОЧНУЮ ГАЗОВУЮ СМЕСЬ (CRM A7.1.6)

Баллон № 9814
Тип, материал баллона LUXFER, алюминий
Вместимость 10 дм^3

Компонент	~~Молярная~~ / Объемная / ~~Массовая~~ доля компонента		Расширенная неопределенность*
	%	млн$^{-1}$	
оксид углерода [CO]	0,0508		0,0025
диоксид серы [SO$_2$]	0,00402		0,00020
оксид азота [NO]	0,0104		0,0005
азот [N$_2$]	остальное		

Аттестованные значения прослеживаются к государственному первичному эталону единиц молярной доли, массовой доли и массовой концентрации компонентов в газовых и газоконденсатных средах (ГЭТ 154-2016).
Дополнительные сведения:
Назначение стандартного образца (СО) и сведения о его прослеживаемости указаны в описании типа СО (см. www.fundmetrology.ru). Указания по хранению и эксплуатации приведены в приложении к данному паспорту.
* - при коэф. охвата k=2, соответствует границам абсолютной погрешности при доверительной вероятности P=0,95.

Давление в баллоне 9,5 МПа
Токсичный компонент есть / ~~нет~~
Смесь воспламеняется ~~да~~ / нет
Дата выпуска 11.04.2018 г.
Действительно по 11.04.2019 г.
Поверочная газовая смесь выпускается по ТУ 2114-014-20810646-2014.
Разряд: ~~нулевой~~ / ~~первый~~ / второй

Начальник отдела аттестации /Павлов М.В./

Оператор сектора метрологии и паспортизации /Зудина С.В./

Поверочная газовая смесь соответствует утвержденному типу стандартного образца состава искусственной газовой смеси на основе химически активных газов (ХА-М-2)

ГСО 10547-2014

СО признан в качестве межгосударственного стандартного образца (МСО) решением МГС от 10.12.2015, протокол № 48-2015, внесен в реестр МСО под № 1999:2015 и допускается к применению без ограничений в Азербайджанской Республике, Республике Армения, Республике Казахстан, Республике Молдова, Республике Узбекистан.

Комплекс производства ПГС ООО «МОНИТОРИНГ» аккредитован в соответствии с требованиями Международного стандарта Руководство ИСО 34:2009 (ISO Guide 34).
Аттестат аккредитации № AAC.RM.00284, действителен до 27.07.2019 г.

Лицензия № ВХ-19-005994 от 01.11.17. на эксплуатацию ОПО I,II,III кл.

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 (www.comde-derenda.com) 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 conductec 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.

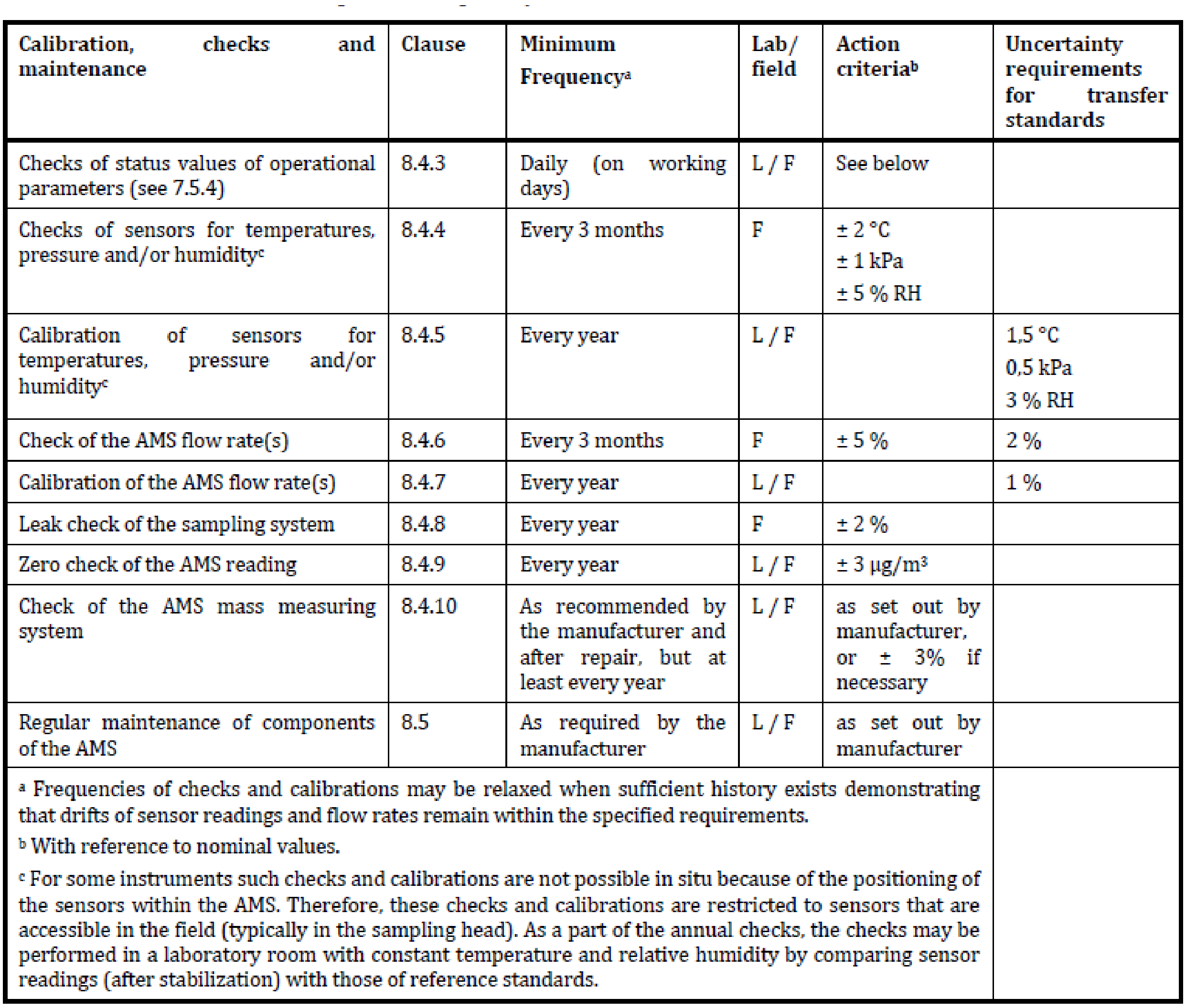
The next step is the first weighing series, which consists of weighing the unladen filters, usually in two weighing passes. All the selected filters are thus consecutively weighed once and then for a second time. If discrepancies lying outside the specified tolerances are recorded between the first and 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 → coding station → balance → 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**[a]	**Lab/ field**	**Action criteria**[b]	**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[c]	8.4.4	Every 3 months	F	± 2 °C ± 1 kPa ± 5 % RH	
Calibration of sensors for temperatures, pressure and/or humidity[c]	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	

[a] 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.

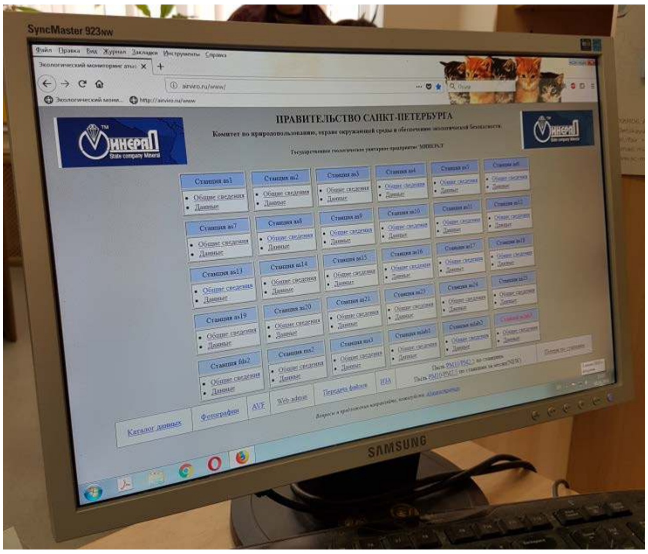
[c] For some instruments such checks and calibrations are not possible in situ because of the positioning of the sensors within the AMS. Therefore, these checks and calibrations are restricted to sensors that are accessible in the field (typically in the sampling head). As a part of the annual checks, 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.

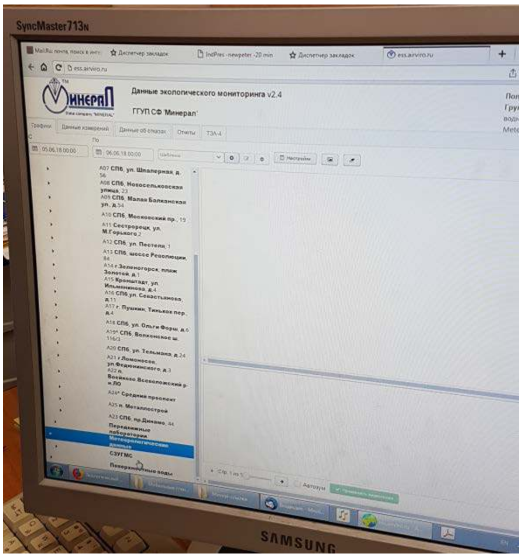
8. Data collection

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:

РОСАККРЕДИТАЦИЯ

ФЕДЕРАЛЬНАЯ СЛУЖБА ПО АККРЕДИТАЦИИ № 0002796

АТТЕСТАТ АККРЕДИТАЦИИ

№ RA.RU.515825 выдан 21 августа 2015 г.
номер аттестата аккредитации и дата выдачи

Настоящий аттестат выдан Санкт-Петербургскому государственному геологическому унитарному предприятию "Специализированная фирма "Минерал"; ИНН:7817009067
199106, Санкт-Петербург, Детская ул., д. 26, лит. А. пом. 4 н
место нахождения (место жительства) заявителя

и удостоверяет, что Лаборатория экологического мониторинга Санкт-Петербургского государственного геологического унитарного предприятия "Специализированная фирма "Минерал"
199155, Санкт-Петербург, пр. КИМа. 26, лит. А, пом. 1н
адрес места (мест) осуществления деятельности

соответствует требованиям ГОСТ ИСО/МЭК 17025-2009

аккредитован(о) в качестве Испытательной лаборатории (центра)

в соответствии с областью аккредитации, область аккредитации определена в приложении к настоящему аттестату и является неотъемлемой частью аттестата.

Дата внесения сведений в реестр аккредитованных лиц 11 августа 2015 г.

М.П.

Руководитель (заместитель Руководителя)
Федеральной службы по аккредитации
подпись
М.А. Якутова
инициалы, фамилия

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

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 43С Thermo Electron. Инструкция по эксплуатации.

6. Газоанализатор оксидов азота и диоксида азота модель 42С Thermo Electron. Инструкция по эксплуатации.

7. Газоанализатор оксида углерода модель 48С 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, CO12M. Техническое руководство.

12. Хемилюминесцентный анализатор окиси азота, модуль AC32M. Техническое руководство.

13. УФ фотометрический анализатор озона, модуль O342M. Техническое руководство.

14. УФ флуоресцентный анализатор двуокиси серы, AF22M. 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-PCXR8 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.

21. 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.
1.3. 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
2.1. Участок технического обслуживания газоанализаторов и вспомогательного оборудования
2.1.1. Порядок проведения диагностики, профилактических и ремонтных работ газоанализаторов и устройств системы автоматического пробоотбора взвешенных частиц
2.1.2. Порядок проведения диагностики, профилактических и ремонтных работ поверочного оборудования
2.1.3. Регламентное обслуживание метеорологического оборудования
2.1.4. Регламентное обслуживание вспомогательного оборудования
2.2. Технологический участок отбора проб на фильтры, сорбенты и анализа ЛОС
2.2.1. 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
2.2.6. Порядок проведения измерений для определения ЛОС с использованием пробоотборных пакетов
2.2.7. Регламентное обслуживание системы AWS-1
2.2.8. 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.
5. Инструкция по анализу проб воздуха с использованием пробоотборных пакетов на газовом хроматографе Synspec GC 955 600.
6. 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.