



Project of Strategic Interest NextData

Deliverable D1.2.2

Feasibility of upgrade actions for measurement stations within GAW-WMO

Resp: Angela Marinoni, CNR-ISAC

Table of Contents

1. FEASIBILITY STUDY FOR THE INSTALLATION OF A WAVELENGTH-SCAN CAVITY RING DOWN SPECTROSCOPY (WS-CRDS) IN REMOTE MEASUREMENT STATIONS	4
1.1 INTRODUCTION.....	4
1.2 WAVELENGTH SCANNING – CAVITY RING DOWN SPECTROSCOPY (WS-CRDS)	4
1.3 THE MEASUREMENT SYSTEM: PICARRO G2401	4
1.4 ISSUES FOR MEASUREMENT IMPLEMENTATION	6
1.5 DEFINITION OF STRATEGY FOR ROUTINE CALIBRATIONS	7
1.6 ESTIMATED COSTS FOR SETUP.....	8
1.7 CONCLUSIONS	9
1.8 REFERENCES	9
2. FEASIBILITY STUDY FOR THE UPGRADE OF A COMMERCIAL CARBON MONOXIDE ANALYZER IN REMOTE MEASUREMENT STATIONS.....	10
2.1 INTRODUCTION.....	10
2.2 EXPERIMENTAL SETUP	10
2.3 EVALUATION OF MEASUREMENT UNCERTAINTY	12
2.4 INSTRUMENT ROUTINE CHECKS.....	15
2.5 DILUTION CALCULATION	15
2.6 EQUIPMENT SPECIFICATION AND ESTIMATED COSTS.....	16
2.7 CONCLUSIONS	16
2.8 REFERENCES	16
3. FEASIBILITY STUDY FOR THE INSTALLATION OF NOX MEASUREMENT SYSTEMS IN REMOTE MEASUREMENT STATIONS	17
3.1 INTRODUCTION.....	17
3.2 CHEMILUMINESCENCE DETECTION (CLD)	19
3.3 ISSUES FOR MEASUREMENT IMPLEMENTATION	20
3.4 DEFINITION OF STRATEGY FOR ROUTINE CALIBRATIONS	21
3.5 ESTIMATED SET-UP COSTS	22
3.6 CONCLUSIONS	22
3.7 REFERENCES	23
4. FEASIBILITY STUDY FOR THE UPGRADE OF THE SAMPLING SYSTEM OF A COMMERCIAL INSTRUMENT FOR THE ON-LINE MONITORING OF PM1 AND PM10	24
4.1 INTRODUCTION.....	24
4.2 EXPERIMENTAL SET-UP.....	24
4.3 PRELIMINARY RESULTS	25
4.3.1 Description of implementation	26

4.4 CONCLUSION (PRELIMINARY) 27

4.5 REFERENCES 27

5. FEASIBILITY STUDY FOR THE INSTALLATION OF AN AEROSOL LIDAR AT THE GAW-WMO GLOBAL STATION “O. VITTORI” AT MT. CIMONE.....29

5.1 INTRODUCTION..... 29

5.2 EXPERIMENTAL SET-UP 30

5.2.1 *System description*.....30

5.2.2 *Acquisition system*.....32

5.3 RESULTS 32

5.3.1 *Study of system sensitivity to sunlight*.....32

5.3.2 *Performance evaluation*.....33

5.4 CONCLUSIONS 37

5.5 REFERENCES 37

1. FEASIBILITY STUDY FOR THE INSTALLATION OF A WAVELENGTH-SCAN CAVITY RING DOWN SPECTROSCOPY (WS-CRDS) IN REMOTE MEASUREMENT STATIONS

1.1 INTRODUCTION

In the recent past, Non-Dispersive Infrared (NDIR) absorption and gas-chromatography (GC), represented one of the most widely employed techniques for the continuous and accurate measurements of carbon dioxide (CO₂) and methane (CH₄), the two well-mixed GHGs being characterised by the highest global radiative forcing (IPCC, 2007). Even if characterised by elevated measurement accuracy, these systems are nevertheless very difficult to operate: continuous and large efforts in terms of skilled manpower, consumables and maintenance are required in order to assure long-term reliable observations. Moreover, other instruments should generally be used to obtain simultaneous measurements of CO₂ and CH₄.

The present report provides a summary of a preliminary study aiming to evaluate the feasibility of the implementation of Wavelength Scanning – Cavity Ring Down Spectroscopy (WS-CRDS) systems at remote atmospheric observatories. To this end, a visit was undertaken to the laboratories of the World Calibration Centre for surface ozone, carbon monoxide, methane of GAW-WMO hosted by EMPA – Swiss Federal Institute for Research and Technology (Zurich).

In particular, a brief description of the WS-CRDS technique will be provided. Specifically, discussions focused on the Picarro G2401 WS-CRDS, the only existing commercial instrument able to perform simultaneous measurements of CO₂, CH₄ and CO along with water vapour mixing ratio. Since CO plays an important role in the oxidation/reduction chemistry of the atmosphere, and is a very efficient tracer of pollutant emissions, the simultaneous detection of CO with greenhouse gases represents a very powerful tool to better understand greenhouse gas variability and mixing ratio trends.

A survey of possible critical points in the instrument implementation is presented, also taking into account applicative solutions for setting up an optimal measurement system. Calibration issues and strategies are then considered. Finally, a provisional estimate of the budget necessary for starting the measurement programme is outlined.

1.2 WAVELENGTH SCANNING – CAVITY RING DOWN SPECTROSCOPY (WS-CRDS)

WS-CRDS currently represents the state-of-the-art system for continuous and simultaneous determination of CO₂, CH₄, CO and water vapour atmospheric mixing ratios. A detailed description of the WS-CRDS technology is given by Crosson (2008). The WS-CRDS can measure CO₂, CH₄, CO and H₂O simultaneously, based on the laser absorption spectroscopy. Essentially, the WS-CRDS setup is composed of 1) a laser source, 2) a high-precision wavelength monitor, 3) an optical cavity, 4) a photo detector, and, 5) a data processing computer.

The difference in the decay time (the so-called “ring-down”) of the laser signal with and without absorption by the analysed molecules, is proportional to the mole fraction of the single atmospheric compound, and allows an accurate determination of its mixing ratio. The instrument is equipped with an enhanced system for laser wavelength control, which in a very short time switches the laser from a wavelength where the target gases absorb, to a wavelength where no absorption occurs. In the latter case, the signal decay is only related to the (small) leak across the mirrors.

1.3 THE MEASUREMENT SYSTEM: PICARRO G2401

For the specific instrument considered (Picarro G2401), the air sample is supplied to the optical cavity using a diaphragm pump. A laser light at wavelengths specific for the atmospheric compounds to be

determined (CO_2 , CH_4 , CO or water vapour) is emitted into the optical cavity. When the photo-detector achieves a steady signal, the laser is immediately shut off. The optical cavity is equipped with three high-reflectivity mirrors with cavity pressure and temperature kept at 140.00 ± 0.05 Torr and 45.00 ± 0.01 °C. Due to the high reflectivity of the mirrors, an effective optical path length of about 20 km is achieved inside the detection chamber. The Picarro G2401 determines the intensity of the light over the gas absorption line, using a high-precision wavelength monitor (resolution: 0.0003 cm^{-1}). Near-infrared radiation ($1.55 - 1.65 \text{ }\mu\text{m}$) is used to detect CO_2 , CH_4 , CO and water vapour. The analytical precision of CO_2 and CH_4 for the 5 min average, typically obtained by WS-CRDS instruments, is 0.05 ppm and 0.3 ppb (Rella et al., 2012), while for CO a precision of 1.0 ppb is achieved for 10 min averaging (Zelwegger et al., 2012).

The Picarro G2401 WS-CRG is a compact instrument ($43.18 \times 17.78 \times 44.57 \text{ cm}$), characterised by a relatively low weight (27 kg) that makes it suitable for transportation to remote locations and installation in equipped laboratories at remote observatories (see Figure 1.1). It is also characterised by limited power consumption (110 W, 260 W at start-up), even considering the power required for the external pump (35 W) that guarantees the sampling flow across the instrument. It is equipped with an internal PC with dual-core processor which hosts the software for data acquisition and calibration procedures. It is possible to connect the instrument directly to an Ethernet connection, which allows for near real time data download and remote control of the system (even by the Manufacturer). Based on previous experimental experiences (Steinbacher et al., 2011), in agreement with the manufacturer's data sheet, this instrument is suitable for use in long-term monitoring at high-mountain sites. However, at very low ambient pressure (typically less than 600 hPa), the system may give rise to unexpected problems that cannot be foreseen in advance. In maritime environments (with high content of sea salt in atmospheric aerosol) or in regions strongly affected by mineral dust, an external anti-particulate filter (stainless steel AISI316) is required to avoid contamination of the cavity chamber. The filter requires regular inspection and, in the case of necessity, should be changed.



Figure 1.1. Picarro G2401 WS-CRDS instrument at the World Calibration Center for ozone, methane and carbon monoxide of the Global Atmosphere Watch, hosted at EMPA (Zurich)

A further strength of this system is its independence from ambient temperature variations (at daily or longer/shorter time scales), thanks to a very efficient control of temperature of the cavity cell. Although installation of the instrument in a laboratory with control of ambient (room) temperature is appropriate, the Picarro G2401 is known to perform well also in the presence of significant temperature variations. It is

nevertheless recommended to maintain the laboratory temperature below 45°C: problems can occur if the ambient temperature is higher than the internal temperature of the cavity chamber. Exposure of the instrument to direct sunlight is also recommended.

The Picarro G2401 considered was equipped with a self-built unity control for the management of routine calibrations and sampling. It is mandatory to implement a similar system also at remote stations to guarantee the correct execution of calibrations (use of working and calibration standards, analysis of target standards). The basic elements of the system (to set between the instrument inlet and the calibration/sampling lines) are: 1) a multi-input valve, 2) a flow controller, and, 3) a three way valve with a solenoid.

- 1) The best solution is to use a valve with at least 5 inputs: n.1 (plugged) for sampling, n.2 for the target standard and the remaining (n. 3) for working standards. The use of valves with more inputs (e.g. 10) is recommended for directly connecting also the calibration standards or for making some inputs available in case of auditing. Good performance can be achieved using VICI© valves that can be directly connected and managed by the Picarro software.
- 2) After the valve, with the aim of managing the flushing of standard gases, a flow control is needed by needle valve, critical orifice or mass flow controller. The use of the mass flow controller is preferred because, in this case, it is possible to set the flow in a very accurate and stable way. Moreover, any flow change can be more easily accomplished even by remote: to this end, the controller software can be directly installed on the Picarro internal PC. Finally, in the case of using a mass flow controller, the flow data can be stored for QA/QC purposes.
- 3) Finally, a three way valve is required to switch the flow to the instrument between the calibration and sample outputs.

1.4 ISSUES FOR MEASUREMENT IMPLEMENTATION

A list of “critical” points, very important for a correct implementation of continuous measurements, is provided.

- 1) Based on previous experimental experience, each instrument has its own special features. Thus, accurate laboratory tests are recommended prior to installing the system (e.g. comparison with standard, test to evaluate the influence of water vapour to the mixing ratios readings). Additionally, during the first phase of utilization, it is recommended to perform frequent (i.e 48 hours) comparisons against working standards to evaluate the behaviour of each measurement (CO₂, CH₄, CO) as a function of the instrument.
- 2) Even if the instrument should provide dry mixing ratios for the detected compounds, as described by Chen et al. (2012) and Zelwegger et al (2012), the influence of water vapour on the CO reading can constitute an issue. Here, a test to evaluate the possible artefacts relating to water vapour to the CO mixing ratio, is presented. Basically, as reported in Figure 1.2, it is suggested to inject a few ml of ultrapure water in the sampling line (not directly in the inlet instrument! Add an overflow at the instrument inlet to avoid too many water droplets entering the instrument!) and leave it to vaporize for a few minutes, or insert saturated silica gel inside the anti-particulate filter and leave it to desorb water vapour for about 24 hours. In this way, thanks to the accurate water vapour mixing ratio measurements carried out by the instrument, it is possible to relate the presence of water vapour around 2-3% to CO (and to the other compounds). In the event of significant influence being detected, a drying system (e.g. nafion© tube, see the work by Welp et al., 2012) is needed to obtain accurate measurements. In this case, attention must be paid as water vapour can be desorbed from

the nafion© walls when dry working standards or calibration standards are used: this creates interferences with the gas reading. It is a point that can represent an issue in wet environments.

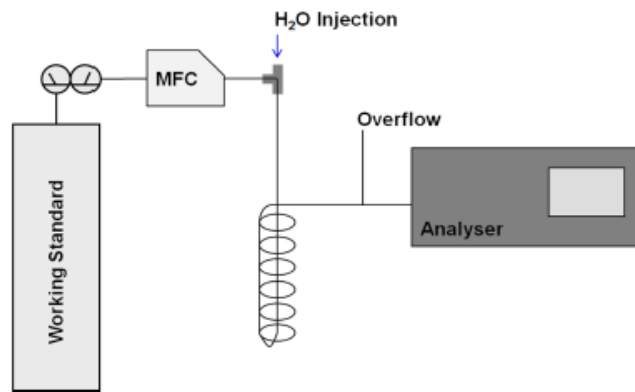


Figure 1.2. Experimental setup for the determination of the water vapour interference (courtesy by Zelwegger et al., 2012)

- 3) It is strongly recommended to have an image of the hard disk to avoid loss of data and settings, as well as to remount the system in the case of HD crash.
- 4) The external pump provided by the manufacturer is not specifically designed for working at high altitudes (low pressure environments) or maritime sites (even lower pressure). It is thus recommended to substitute the original pump with a high quality pump with flow regulation to meet the flow needed by the instrument (0.4 l/min). This is a very important point as the stopping of the pump can seriously damage the cavity chamber due to pressure drop. Thus, also the pump should be provided by UPS to guarantee power continuity in any conditions. Moreover, the pump must be switched on before the instrument and switched off afterwards.
- 5) For sampling lines, it is recommended to use stainless steel or decabon© in conjunction with Svagelok© (or similar) fittings for connections. Should a centralized sampling head not be available with sufficient flow to ensure a suitable flow throughout the measurement chamber and minimize the residence time of the air stream in the sampling systems, it is also recommended to have an additional pump with an extra-flux (total flux: 2-3 l/min) before the inlet of the instrument, to guarantee sampling at ambient pressure.
- 6) Among the single instruments, some differences can be present concerning the acquisition of data, due to slightly different versions of the software mounted on the interval PC.

1.5 DEFINITION OF STRATEGY FOR ROUTINE CALIBRATIONS

To obtain a set of measurements with an accuracy able to meet the requirements by GAW/WMO (see WMO, 2009), a well-designed calibration system with a set of working standards, target gas and calibration standards is necessary.

Since the instrument response to mixing ratio variations is highly linear, it is sufficient to have at least 2 (or better 3) different mixing ratios available in the used working standards. Moreover, a system for zero air generation is recommended both to perform routine zero checks, aimed to verify instrument stability, and to provide a more accurate linear interpolation of the calibration points.

- 1) *ZERO AIR*: The zero air generator should be equipped with an air compressor (oil free), as well as some devices to scrubber the measured compounds and dry the air. For optimal CO₂

removal, a cartridge filled with commercial CO₂ absorber can be inserted in the zero air line just upstream of the instrument input. A further zero check can be performed using ultrapure nitrogen. This also allows the verification of the ZERO air system functioning.

- 2) *WORKING STANDARD*: At least two working standards with CO₂, CH₄ and CO mixing ratios representing upper and lower ranges of the expected ambient variability should be used (higher mixing ratios for CO) with a frequency varying from 48 hours (at the beginning of operation and for more unstable instruments) to 1 month. These calibrations should be performed at different times from one day to another. Avoiding outline calibrations at the same hour of day helps to increase the representativeness of the measurements on daily scales and allows the determination of possible problems occurring at different times of day (e.g. related with laboratory ambient conditions). As the WS/CRDS detects only specific isotopes of the analysed compounds, it is recommended that tanks filled with real ambient air matrix be used as standards (see Nara et al., 2012). To avoid interference of water vapour, this air should be dry. Such working standards can be made at the laboratories hosting the instrument or purchased from commercial laboratories.
- 3) *TARGET GAS*: The target gas is a further standard used to evaluate the stability of measurements after correction against the working standards. It should be provided in a dry real air matrix at a mixing ratio similar to that expected from the observations (higher for CO, e.g. 400-800 ppb).
- 4) *CALIBRATION STANDARDS*: A set composed of at least n.3 calibration standards is mandatory at the station or central calibration facility. Currently, these standards can be purchased from NOAA/GMDL, which provide pressurised tanks with real air matrix. The standards should contain different mixing ratios: one representative of the lower boundary of expected ambient mixing ratios, one representative of the typical average mixing ratios, and one representative for the upper range of expected ambient mixing ratios. These calibration standards should be compared every 6 months against the working standards to evaluate possible drifts of the latter and directly on the instrument to evaluate the stability of calibration factors.

All the standards are usually provided in high pressured cylinders. Thus, the expected consumption can range from a few months years for 20 lt cylinders of working standards (assuming a use of 15 min every 48 hours) to about 5 or more years for calibration standards. In order to minimize the consumption of the working standard, a critical orifice can be inserted at the instrument inlet without modifying the quality of the measurements.

1.6 ESTIMATED COSTS FOR SETUP

In the following we list the estimated costs relating to the feasibility of WS-CRDS installation at a remote or at high mountain site.

- Instrument cost (with external pump and internal PC with acquisition and calibration software): roughly 90.000,00 USD
- External pump (back-up): 3.000,00 Euro
- Additional pump: 1.000,00 Euro
- Controller unit for calibration: 10.000,00 Euro
- Calibration standard (three cylinders): 15.000,00 Euro
- Working standard (two standard): 500,00 Euro
- Target gas (n.1 cylinder): 250,00 Euro

1.7 CONCLUSIONS

Based on the above evidence, the use of commercial CRDS systems appears to be suitable for continuous monitoring of CO₂, CH₄, CO and H₂O at remote high-altitude or maritime observatories, provided that a correct implementation (installation, preliminary tests, routinely calibrations and checks) is performed. The execution of in-situ tests (even during the first phase of measurements) is nevertheless recommendable for indicating specific issues relating to their continuous use in the challenging operative conditions that usually characterise remote measurement sites.

1.8 REFERENCES

- Chen, H., A. Karion, C. W. Rella, J. Winderlich, C. Gerbig, A. Filges, T. Newberger, C. Sweeney, and P. P. Tans, Accurate measurements of carbon monoxide in humid air using the cavity ring-down spectroscopy (CRDS) technique, *Atmos. Meas. Tech. Discuss.*, 5, 6493-6517, 2012.
- Crosson, E. R.: A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor, *Appl. Phys. B-Lasers O.*, 92, 403–408, 2008.
- IPCC, Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, 104 pp, 2007.
- Nara, H., H. Tanimoto, Y. Tohjima, H. Mukai, Y. Nojiri, K. Katsumata, and C. Rella, Evaluation of factors affecting accurate measurements of atmospheric CO₂ and CH₄ by wavelength-scanned cavity ring-down spectroscopy, *Atmos. Meas. Tech. Discuss.*, 5, 5009-5041, 2012
- Steinbacher M., Long-Term Methane Observations at the Global Atmosphere Watch Site Jungfraujoch with Gas Chromatography and Cavity Ringdown Spectroscopy. NOAA ESRL Global Monitoring Annual Conference, June 2011.
- Welp, L. R., R. F. Keeling, R. F. Weiss, W. Paplawsky, and S. Heckman, Design and performance of a Nafion dryer for continuous operation at CO₂ and CH₄ air monitoring sites. *Atmos. Meas. Tech. Discuss.*, 5, 5449-5468, 2012.
- WMO, 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurements Techniques, Jena, Germany, 2009.
- Zellwegger, C., M. Steinbacher, and B. Buchmann, Evaluation of three new laser spectrometer techniques for in-situ carbon monoxide measurements *Atmos. Meas. Tech. Discuss.*, 5, 4735-4769, 2012

2. FEASIBILITY STUDY FOR THE UPGRADE OF A COMMERCIAL CARBON MONOXIDE ANALYZER IN REMOTE MEASUREMENT STATIONS

2.1 INTRODUCTION

Carbon Monoxide (CO) plays an important role in the oxidation/reduction chemistry of the atmosphere. Therefore, CO distributions and trends are key variables for improving our understanding of the Earth's present and future atmosphere. CO has an indirect radiative forcing effect by influencing atmospheric mixing ratios of methane and tropospheric ozone through chemical reactions with other atmospheric constituents (e.g. the hydroxyl radical OH) that would otherwise destroy them. Through natural processes in the atmosphere, CO is eventually oxidized to carbon dioxide. Currently, the two “golden” technologies for the in-situ continuous determination of atmospheric CO mixing ratios are gas-chromatography (GC) and Cavity Ring Down Spectroscopy (CRDS). Nevertheless, these instrumental set-up are very expensive in terms of economic expenditure (GC and CRDS), highly skilled man power and consumables (GC). In particular, GC systems incur the running costs of the large consumption of carrier gas cylinders. Thus, in the framework of the project activity, at the ICO-OV Global GAW Station, a feasibility study was performed to upgrade a commercial CO analyzer, using gas filter correlation and NDIR (Non Dispersive Infra-Red absorption) technology, able to perform continuous measurements. This kind of instrumentation is much less expensive than GC or CRDS systems, is robust and requires only basic care for operation and maintenance. Moreover GC systems, due to the complexity of the measurement processes, usually provide a few observations per hour, thus reducing the measurement representativeness, especially in cases of small and rapid mixing ratio variations. Conversely, NDIR systems provide CO mixing ratio with very high time frequency (few tenths of seconds). Thus, such systems appear to be suitable for installation in remote observatories, where it is not possible to have personnel continuously on duty, also if a limited amount of funds is available for the implementation of CO measurements. Nevertheless, NDIR systems can have some issues related with possible interference of water vapor during the detection of CO and the dependency of zero signal on ambient working temperature.

In this report, we provide a description of a feasibility study, implemented at the “O. Vittori” Observatory of the Mt. Cimone GAW-WMO Global Station, for upgrading a commercial CO NDIR analyzer based on the previous experience of Henne et al. (2008). With the aim of disseminating our experience to other Italian remote atmospheric observatories within GAW-WMO and SHARE networks, the experimental set-up is also described, an indicative budget required for implementing a similar measurement programme is also presented, along with a basic list of standard operation procedures (SOP) that should be followed for a correct execution of measurements.

2.2 EXPERIMENTAL SETUP

The instrument considered in this feasibility study is a CO monitor Thermo Electron 48C-TL, already available at the station. The instrument uses gas filter correlation and NDIR technology for determining CO ambient concentration (expressed as nmol/mol). Ambient air is drawn in the instrument using the internal pump at 1.0 l/min and the instrument is connected to a glass manifold with approx. 1.5 m of Teflon tube. At the ICO-OV GAW-WMO Global Station, the glass manifold is part of the trace gas glass inlet (main flux: 100 l/s), extending 1.5 m above the roof of the station. The experimental setup used for the feasibility study is reported in Figure 2.1.

To minimize the possible influence of water vapor in NDIR detection, the ambient air passes through a drying system (Nafion® Dryer) and is then injected into the measurement cell. The exhaust from the measurement cell is used as drying flow of the Nafion® Dryer exchange system. The system is also equipped with a purge air unit (composed of a Parker drying system and steel tube filled with Sofnocat

423). It is recommended to use the purging (flow:~ 140 ml/min, pressure: 15 Psig) to flush the gas correlation wheel, thus reducing possible interference due to contaminants, and therefore increasing measurement reliability.

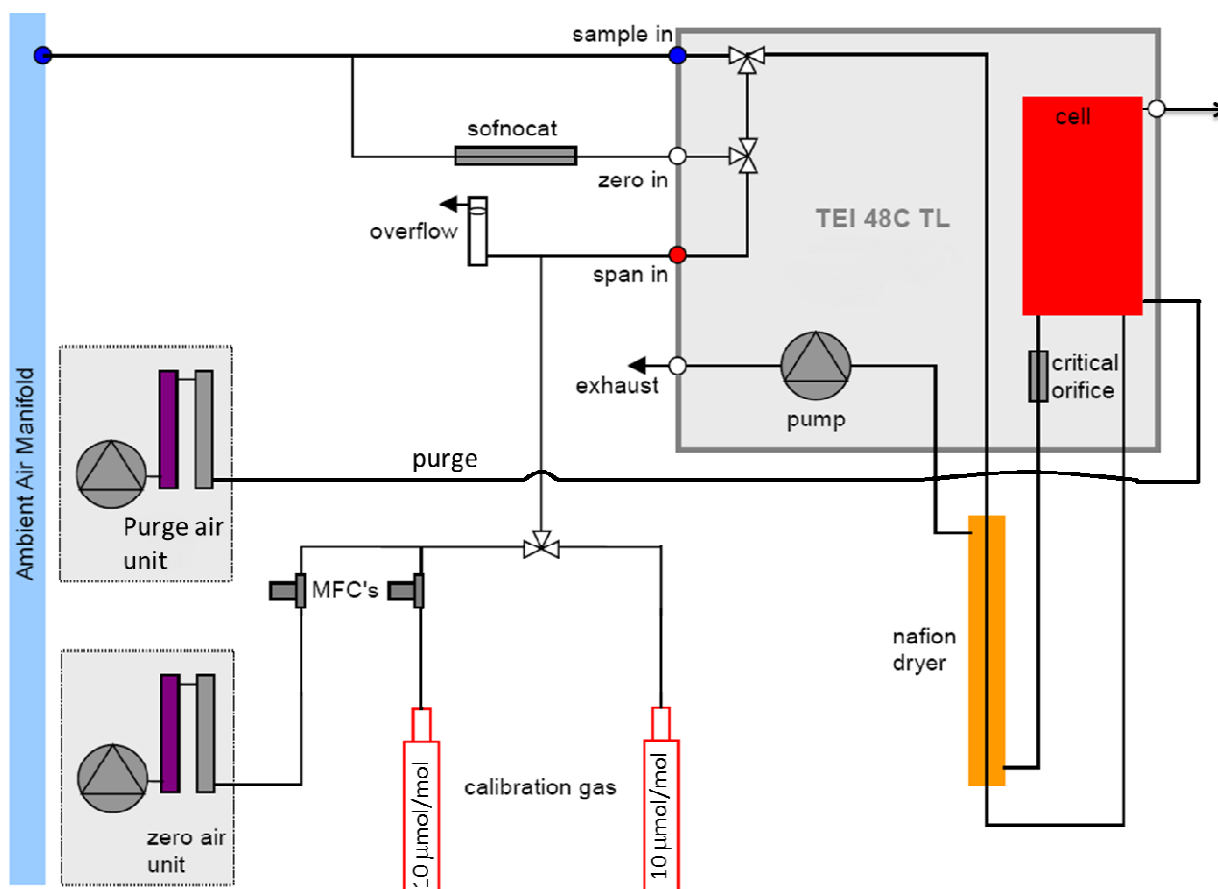


Figure 2.1. Instrumental setup of the feasibility study at ICO-OV GAW-WMO Global Station.

The Thermo 48C-TL instrument is characterized by a strong drift of the zero value, due to changes in ambient (room) temperature: to minimize the influence of temperature on measurements, a specific software was designed and used to control the zero calibration, forcing the instrument to perform calibration every 30 minute (the zero calibration minimum time interval, as stated by the manufacturer is 2 hours).

The zero air necessary for the zero calibration is obtained using a steel tube containing Sofnocat 423. Due to the switching in the instrument internal valves during the zero cycle, the ambient air is forced to pass through Sofnocat ©. The zero air is then injected in the cell for 15 minutes and only the final 5 minutes are averaged to produce the zero value, which is applied to the instrument using the self-built software.

The span calibration is performed once a day, starting at 00:30 AM and ending at 00:45 AM. The span value is 500 nmol/mol, this concentration being obtained from the dilution of a 10 µmol/mol CO standard cylinder (Producer: Messer Italia) with zero air produced by the zero air unit, constituted by carbonate cylinder filled with silica gel (to dry the ambient air) and a steel tube containing Sofnocat© 423. Appendix A reports the calculation used to derive the final concentration from the standard cylinder. The standard and zero air flows are regulated using two Mass Flow Controller (MFC) (Producer: Brook Instrument Ltd)

with different operative ranges: the one regulating zero air flow works between 0 and 5000 l/min, while the one regulating the standard flow works between 0 and 500 l/min.

Two electronically controlled valves are installed upstream of the two MFCs, so that the system can be completely controlled in the case of failures. Additionally, in this way, the two MFCs (and the valves) are normally closed and opened only when there is the need for span calibration, increasing the stability of the MFCs calibration as well as the MCF life time.

The span flow is over the normal 1 l/min sampling flow, so that the lines are slightly over-pressurized, preventing ambient air to be sucked into the instrument during calibration. However, to compensate for the over-pressure, an overflow “T-tube” is installed just before the diluted flow enters the instrument.

2.3 EVALUATION OF MEASUREMENT UNCERTAINTY

To evaluate the effectiveness of the implementation, the uncertainty of the CO measurement was calculated on a monthly basis using a statistical approach, in view of the high number of data available. In particular, the measurement uncertainty was evaluated using a certified CO standard at 500 nmol/mol (span check). To assess the presence of random and systematic errors, two quantities are calculated:

1. The difference between the observed span data and the 500 nmol/mol span value (the standard deviation of the span data also provides a measure of the measurement precision for this mixing ratio).
2. The difference between the observed span data and the respective monthly average value (assumed as the “true” value of the span mixing ratio).

The distribution of the two quantities (Figure 2.2 and 2.3) indicates the predominance of random errors (with respect to systematic errors) in the measurement of the span values.

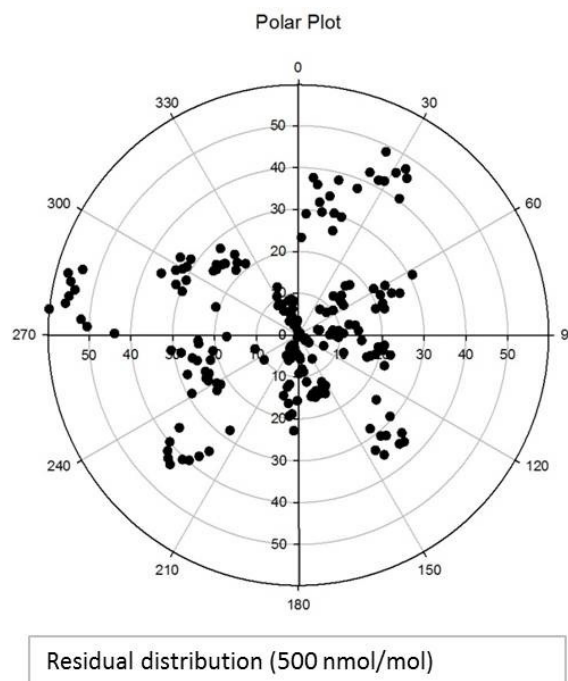


Figure 2.2. Distribution of the differences between the span data and the expected value of 500 nmol/mol. September 2012 data are shown in the figure.

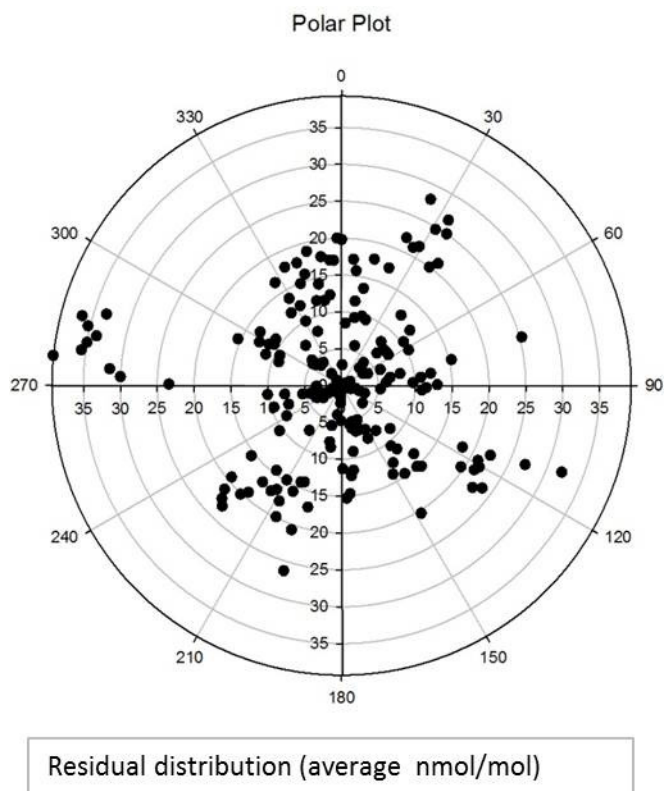


Figure 2.3. Distribution of the difference between the span data and their average value. September 2012 data are shown in the figure (average value of 520.5 nmol/mol).

The accuracy of the measurement, in terms of relative standard deviation over daily repeated analysis of the 500 nmol/mol certified CO standard (15 minutes per day) is 4 %, with a total expanded uncertainty of 8 % ($k=2$).

In order to further assess the effectiveness of the implemented setup, during the period July 12, 2012 and August 3, 2012, a comparison was performed between time series of CO mixing ratio recorded by the NDIR system and those recorded by a GC system (equipped with a Flame Ionization Detector). Both systems were sampling external air from the centralized sampling system working at the station. The statistical analysis of the data is reported in Table 2.1 and the result of the linear correlation analysis is reported in Figure 2.4.

	GC-FID (nmol/mol)	NDIR (nmol/mol)
N° Data	959	1045
Average	104.42	121.79
Standard Deviation	14.99	17.59
5th percentile	79.54	93.48
25th percentile	95.77	110.74
50th percentile	102.97	120.63
75th percentile	113.53	133.45
95th percentile	130.62	152.92

Table 2.1. Statistical analysis of CO measurements carried out using two different techniques (Gas Chromatography and Gas Filter Correlation) in the period 12/07/2012 - 03/08/2012 at ICO-OV.

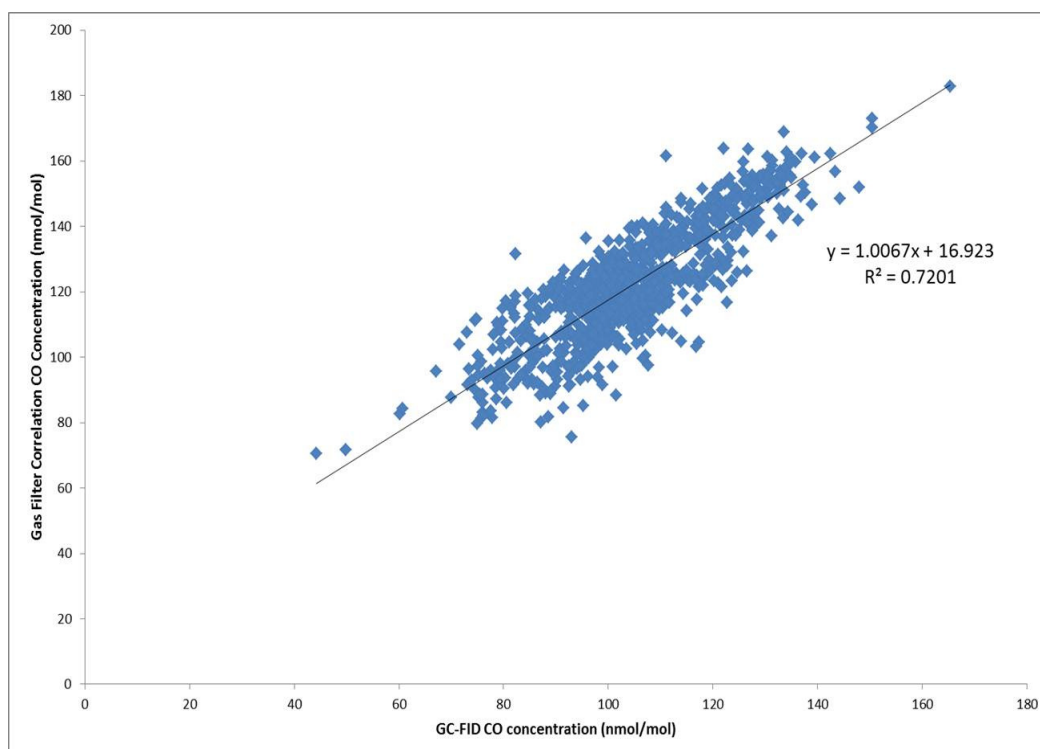


Figure 2.4. Linear correlation between the CO mixing ratio measured using a GC-FID system (X Axis) and a Gas Filter Correlation system (Y Axis). The data refer to the ambient mixing ratios measured at ICO-OV in the period 12/07/2012 - 03/08/2012.

The results showed that, although a bias of 16.92 nmol/mol was detected between the two measurement systems (higher mixing ratio for NDIR), a significant linear correlation existed between the two time series. This result indicates that (giving an accurate calibration to determine and correct *bias*), NDIR and GC-FID systems showed a good consistency and a comparable extended uncertainty (see Table 2.1).

2.4 INSTRUMENT ROUTINE CHECKS

The routine checks that should be performed for an accurate execution of CO monitoring by the implemented NDIR system are as follows:

- Check the pressure of the CO standard cylinder: as reported by the manufacturer, it should be substituted if the pressure is below 5 bar (starting pressure: 150 bar).
- Check the Parker dryer. If necessary (as shown by the colorimetric display on the upper face of the dryer), substitute the filter by dismounting the main light blue cylinder.
- Check the silica gel. If necessary, substitute and regenerate.
- Check the state and cleanness of the filter housed before the sample inlet.
- Check the flow of the two Mass Flow Controllers: the one regulating CO (full scale 500 l/min, reported on the side of the MFC) should work at 60 ml/min and the other (full scale 5000 l/min, reported on the side of the MFC) should work at 1140 ml/min.

After any major maintenance, the system should be checked for leakages using soap bubbles. All of the listed checks should be performed at least every 2/3 months.

Moreover, every 3 months, a manual calibration of the instrument should be performed: this can be done by injecting the 10 µmol/mol CO standard directly into the instrument, using the secondary line shown in the setup above.

2.5 DILUTION CALCULATION

The 500 nmol/mol span concentration is obtained by the dilution of a 10000 nmol/mol certified CO standard.

The following steps are necessary to derive the desired span concentration:

- We start with a 10000 nmol/mol CO concentration to be diluted to 500 nmol/mol.
- The span flow is 1.2 l/min (so that the system is slightly over-pressurized) or 1200 ml/min.
- The Mass Flow Controller for the CO standard works between 0 and 500 ml/min.
- The Mass Flow Controller for the zero air works between 0 and 5000 ml/min.
- Considering this data the following equation is applied:

$$500 \text{ nmol/mol} : 10000 \text{ nmol/mol} = x \text{ ml/min} : 1200 \text{ ml/min}$$
- Resolving for x yields a value of 60 ml/min, and so we need 60 ml/min of CO standard and 1140 ml/min of zero air.
- The MFCs settings are therefore 12.0 % (for the CO standard MFC) and 22.8% (for the zero air MFC) of their full scale range.

2.6 EQUIPMENT SPECIFICATION AND ESTIMATED COSTS

The following list shows the equipment required for upgrading NDIR CO measurements, according to the present feasibility study:

- Thermo Electron Corporation Gas Filter Correlation CO Analyzer Model 48C-TL : 18500 €.
- Sofnocat 423 (1 Kg - pellets): 1990 pounds Sterling.
- 7601 Air Drier Parker-Balston: 1000 €.
- Brook Instrument Ltd. Mass Flow Controller (0-500 ml/min): 1370 €.
- Brook Instrument Ltd. Mass Flow Controller (0-5000 ml/min): 1370 €.
- CO-Standard Cylinder with a concentration of 10000 nmol/mol (Volume = 50 l, Pressure = 150 bar): 380 € per cylinder plus 827 € per pressure regulator.
- Steel AISI 316 tubes.
- Teflon tubes.
- Silica Gel (for drying the ambient air).

Tubes and silica gel costs are not reported due to differences that strongly depend on specific logistic and technical requirements at different observatories.

2.7 CONCLUSIONS

A commercial NDIR system (Thermo 48C-TL) for determining atmospheric CO mixing ratio has been implemented at the “O. Vittori” Observatory, part of the Mt. Cimone GAW-WMO Global Station. The main intervention was devoted to implementing an efficient automated calibration system able to correct the high zero drift that usually affects this type of instrumentation.

Alongside its robustness, its simple management, the high temporal frequency of measurements, limited power consumption (100W), the results here presented indicate that the implemented NDIR instrument performs satisfactorily. Thus, the implementation of similar systems at remote and high mountain sites, where the CO mixing ratios are fairly low in comparison to those measured at PBL measurement sites, may represent a cheaper solutions compared to the more expensive (both economically and in terms of manpower) GC and CRDS systems.

2.8 REFERENCES

Henne,S., Klausen,J., Junkermann,W., Kariuki,J.M., Aseyo,J.O., and Buchmann,B.: Representativeness and climatology of carbon monoxide and ozone at the global GAW station Mt. Kenya in equatorial Africa, Atmos. Chem. Phys., 8, 3119-3139, doi:10.5194/acp-8-3119-2008, 2008.

3. FEASIBILITY STUDY FOR THE INSTALLATION OF NO_x MEASUREMENT SYSTEMS IN REMOTE MEASUREMENT STATIONS

3.1 INTRODUCTION

The present work provides information on the implementation of continuous nitrogen oxides (NO_x), nitric oxide (NO) and nitrogen dioxide (NO₂) measurements at remote high-mountain stations.

As stated in the framework of GAW-WMO (2011), “measurement of NO_x in the global atmosphere is important since it has a large influence on both tropospheric ozone (O₃) and on the hydroxyl radical (OH)”, thus affecting oxidation properties of the troposphere. NO_x has an indirect influence on the radiative forcing by influencing CH₄ and tropospheric ozone (O₃) mixing ratios. This is particularly important considering that tropospheric O₃ is also a powerful pollutant which is harmful to human health and ecosystems. For these reasons, GAW-WMO (2011) recognised the necessity of establishing a global network for the measurement of oxidized nitrogen compound mixing ratios. In particular, in the first phase of implementation, it is recommended that “the nitrogen programme should focus on high quality measurements of NO and NO₂ in as many locations as possible”. At the current stage, no measurements of NO_x are carried out at the Italian GAW-WMO stations participating in the NextData Project. Thus, the implementation of such measurement programmes would significantly upgrade the observing capacity of these stations, as well as the GAW-WMO observational capability in the high-mountain hot-spot regions. Being located at high altitude or in remote locations, NO_x measurements at these stations can provide a reasonable indication of free tropospheric air composition and the possible impact of long-range transport.

An important issue in performing accurate NO_x measurements is the choice of equipment able to quantify NO₂ correctly. Methods for accurate in-situ NO_x determination are relatively expensive in terms of implementation costs and human effort. All these constraints are maximized at remote measurement stations, which are usually characterised by the lack of permanent in-situ personnel and difficult access.

In the framework of this preliminary study, the feasibility of installing a chemiluminescence detector (CLD) at remote high altitude stations was specifically evaluated. For this purpose, a visit was also made to the laboratories of the World Calibration Centre for surface ozone, carbon monoxide, methane of GAW-WMO hosted by EMPA – Swiss Federal Institute for Research and Technology (Zurich).

The importance of obtaining enhanced NO_x measurements at high altitude sites becomes clear if we consider the current NO_x measurements carried out at the “O. Vittori” Observatory, part of the GAW-WMO Global Station at Monte Cimone. Here, continuous NO_x (NO+NO₂) measurements are performed using a commercial “basic” CLD instrument (Thermo 42) with Molybdenum heated converter. No routine calibrations are performed and only zero checks are manually undertaken every 2-3 weeks. As deduced from an analysis of zero signal, the detection limits of this instrument was estimated to be 0.12 ppb for NO and 0.13 ppb for NO_x (2012), i.e. significantly higher than the data quality objective defined by GAW-WMO for similar measurement sites (Tab. 3.1). Figure 3.1 reports the time series of NO, NO₂ and NO_x at Mt. Cimone for a warm month (August) and a cold month (November) in 2012. Even if significant variability of NO_x was evident during August 2012, due to the transport of polluted air-masses from the regional boundary layer, a significant fraction of data (especially for NO) are well below the detection limit. At times, even negative NO values were observed, which implied inconsistent NO_x/NO₂ values (i.e. [NO₂] > [NO_x]). The necessity of using an “enhanced” experimental set-up is even more evident for data recorded during November, 2012. Due to the stronger decoupling between the free troposphere and regional PBL, direct transport of polluted air masses to the measurement site are less likely and NO values are below the detection limit for the most of time. From these data, it is also possible to note that at remote/background

measurement site most NO_x are accounted for by NO₂ or by interference of other NO_y. Thus, an accurate determination of NO₂ mixing ratio is mandatory for an accurate NO_x monitoring at high-mountain stations.

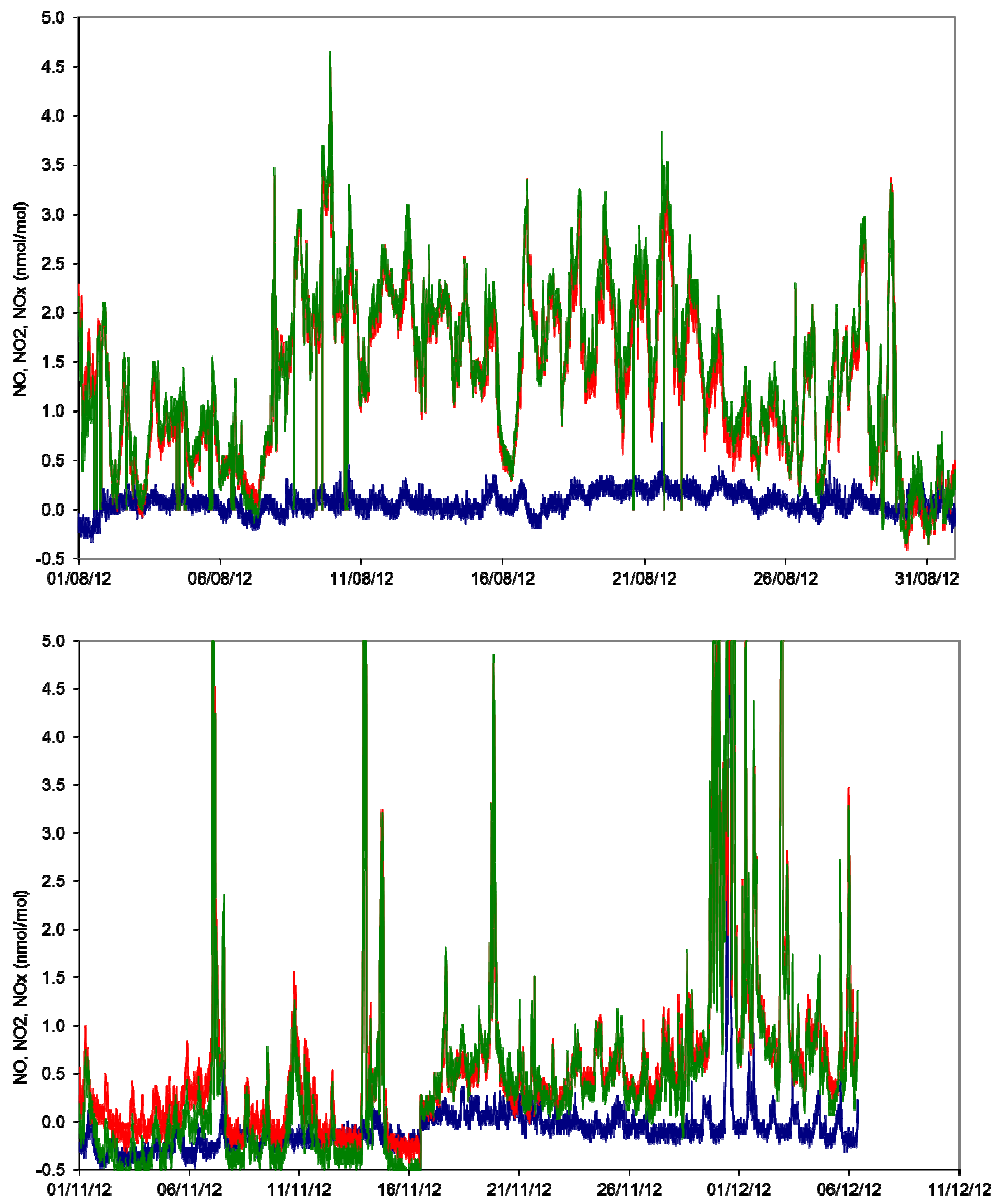


Figure 3.1. Time series (raw data) of NO (blue), NO₂ (red) and NO_x (green) at the Monte Cimone GAW-WMO Global Station for 2012, August (upper plate) and November (bottom plate).

In this work, the upgrade of an “enhanced” commercial NO_x analyser for installation in remote high mountain stations will be described. Firstly, a description of the CLD technique we will provide. Subsequently, the discussion specifically focuses on the implementation of a commercial system (Thermo Scientific 42i) with a photolytic converter (Blue Light Converter), able to selectively determine NO₂. In particular, attention will be paid to the typical experimental set-up necessary to meet the data quality objective (DQO) defined in the framework of GAW-WMO programme for “enhanced – level 2” station (see Table 3.1). Calibration issues and strategies are then considered. Finally, an estimate of the budget necessary for starting the measurement programme is presented.

Even if the implementation of “Pristine, marine, background troposphere - Level 3” stations is recommendable for the NextData remote station locations, it is nevertheless clear that the fulfilment of

such requirements imposes unaffordable measurement challenges. In particular, the continuous operation of the extremely advanced research instruments which are needed to meet the “level 3” DQO, appears to be unlikely in remote and semi-automated stations.

Level	1 (basic)	2 (enhanced)	3 (high)
Site characteristics	Continental basic	Continental background	Pristine, marine background, free troposphere
Mean mixing ratio NO _x	> 1 ppb	0.1 – 1 ppb	< 0.1 ppb
Scope (corresponding time resolution)	long term monitoring, trends (1 hour) source-receptor-relationship, transport processes (hour-minute) photochemical process studies (minute)		
Detection Limit (1 hour, 3-σ)	NO: 50 ppt NO ₂ :100 ppt	NO: 10 ppt NO ₂ :20 ppt	NO: 1 ppt NO ₂ :5 ppt
uncertainty (1 hour, 2-σ) ¹	NO: 40 ppt or 3% NO ₂ :80 ppt or 5%	NO: 8 ppt or 3% NO ₂ :15 ppt or 5%	NO: 1 ppt or 3% NO ₂ :3 ppt or 5%
uncertainty (1 month, 2-σ) ²	NO: 2.5% NO ₂ : 3%	NO: 2.5% NO ₂ : 3%	NO: 1 ppt or 2.5% NO ₂ :3 ppt or 3%
data coverage	66%		
suggested method	CLD / PLC	CLD / PLC	CLD / PLC
alternative method (backup or QC reasons)	CRDS, LIF ; DOAS ; TDLAS	CRDS, LIF ; TDLAS	LIF

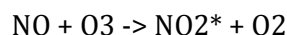
¹ whichever is the larger, e.g. for level 2 “enhanced” at NO₂ of 1 ppb an uncertainty of 50 ppt is required (5% of 1 ppb), at 0.2 ppb an uncertainty of 15 ppt would be required.

² assuming that the random uncertainties are negligible compared to the calibration uncertainty

Table 3.1 Scientific goals, instrumental techniques, and sensitivity requirements for GAW NO_x sites with different characteristics, including continental, continental background, and pristine marine locations. From GAW-WMO (2011).

3.2 CHEMIOLUMINESCENCE DETECTION (CLD)

The CLD methodology is based on the following reactions, involving NO with O₃:



While most of NO reacting with O₃ leads to ground-state NO₂, a fraction leads to excited NO₂ (NO₂*). Most of the NO₂* decays to ground state by collision with other molecules (e.g. O₂, N₂, water vapour) but a fraction decays by emitting the so-called chemiluminescence radiation.

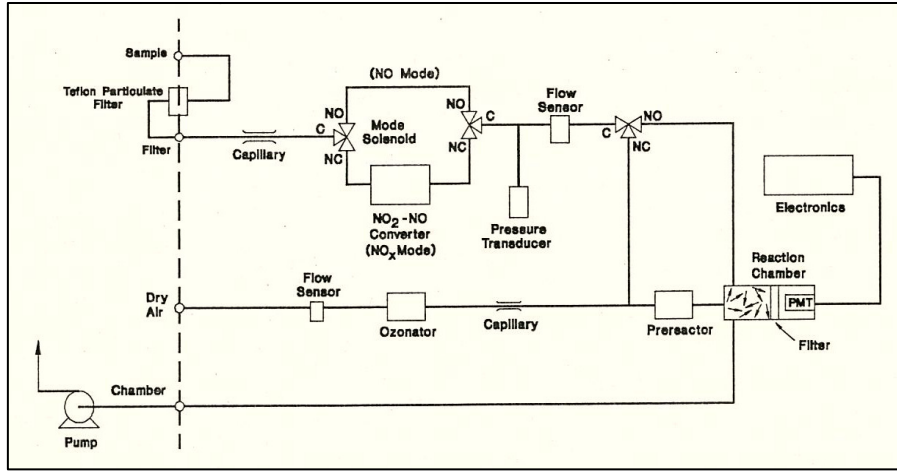


Figure 3.2 Flow scheme of Thermo 42iTL CLD analyzer (courtesy by the ACTRIS Project)

By CLD systems, this chemiluminescence radiation is detected and is proportional to the NO mixing ratio in the analysed air sample. Figure 3.2 reports the flow scheme for the “enhanced” NO_x analyzer considered in this work. Basically, the ambient air is added by an excess of O₃, and chemiluminescence radiation is detected by a photomultiplier tube (PMT) whose temperature is stabilized (usually) below 0°C to minimize signal noise. Since chemiluminescence radiation can also be generated by other interfering compounds (hydrocarbons, like alkenes), the “enhanced” instrumentation should be equipped with a pre-reaction chamber. Here the chemiluminescence emission due to NO occurs, while in the detection chamber only the radiation related with the interfering species is detected. This latter signal is defined as the “detector background signal (DBS)”. Actually, the DBS also encompasses other interference signals. The actual NO mixing ratio is then obtained by subtracting the DBS from the “raw” NO reading.

The CLD is able to detect and quantify only the NO mixing ratio, thus to quantify NO_x (and finally NO₂) mixing ratios, it is necessary to convert NO₂ to NO before quantification. Commercially available instruments for air-quality monitoring are usually equipped with a Molybdenum heated converter. This set-up is not recommended by GAW (2011), since this kind of detector is well-known not to be selective to NO₂: it also converts other oxidized nitrogen compounds, such as nitric acid (HNO₃), peroxyacetyl nitrate (PAN), and other organic nitrates (Steinbacher et al., 2007).

Therefore, the GAW (2011) recommends to implement a photolytic converter instead. This device, which uses an UV light source to photolyze NO₂ to NO, allows a selective conversion of a major fraction (usually with a conversion efficiency – *C_{eff}* - below 80%) of NO₂. After conversion of NO₂ to NO, the signal detected by the CLD is due to the sum of ambient NO plus the fraction of NO₂ converted to NO (NO_{tot}) and the DBS. In particular, the NO₂ mixing ratio is obtained by:

$$NO_2 = \frac{[NO_{tot} - DBS] - [NO - DBS]}{C_{eff}}$$

where DBS is the detector background signal, *C_{eff}* is the conversion efficiency and NO_{tot} is the NO signal after NO₂ conversion.

3.3 ISSUES FOR MEASUREMENT IMPLEMENTATION

The present Section deals with some issues relating to the implementation of NO_x measurements at high-mountain stations.

1) As reported in Section 3, enhanced (trace level) commercial instruments for air quality purposes are usually equipped with Mo converter. Thus, it is necessary to implement them with a photolytic converter. Today, upgrade kits are commercially available (e.g. Blue Light Converter by Air Quality Design Inc.), which can be very easily plugged into a specific analyser. However, some issues should be considered: (i) when replacing the Molybdenum (Mo) converter with a Blue Light Converter (BLC), for optimal functioning it is recommended to ensure ambient (or near ambient) pressure at the BLC, and to gain a higher conversion efficiency; (ii) the different value of conversion efficiency in respect to the original Mo converter (usually between 80% and 100%) should be considered in the signal elaboration and set-up of acquisition software.

2) As indicated in Section 3, DBS, NO and NO₂ measurements are determined by alternating NO (no conversion) and NO_x (conversion) measurement modes. A high time resolution (<10 min) is therefore important to ensure sampling of “uniform” air during subsequent NO and NO_x measurements.

3) The intensity of UV radiation in a photolytic converter decreases with increasing aging of the light source. Estimate of the C_{eff} is a critical point, as this value determines the quantification of NO_x and, hence, NO₂. Therefore, frequent estimates of the C_{eff} are required (see Section 5).

3) During DBS determination, artefacts can occur. Thus, it is recommended (especially at remote sites, where low NO mixing ratios – from few picomol/nol to few nmol/mol - are expected) that regular checks are performed to evaluate this artefact signal (AS). For this purpose, the sample inlet should be overflowed with an excess of zero air, alternating the instrument between sample and background modes. At remote sites, where non local emissions of NO are expected, it is possible to use instead ambient air during night-time, when the NO should be titrated by the ambient O₃. In such conditions, the comparison of the detector background signal to the ambient signal measured should provide a measure of the detector artefact signal (AS). More accurate NO measurements can be achieved by subtracting the DBS and the AS from the actual NO measurement.

4) Due to high NO_x reactivity, the residence time in the inlet lines must be kept as short as possible (less than 5 seconds is recommended).

3.4 DEFINITION OF STRATEGY FOR ROUTINE CALIBRATIONS

Frequent zero and span checks are mandatory in performing accurate NO_x measurements. For “level 2 “ stations, recalibration (NO and NO₂ by calculation of C_{eff}) should be performed every second day, as recommended by GAW (2011). Instrument linearity should be checked up to the span gas concentration at least once a year.

ZERO AIR: zero air (air of sufficiently high purity that the remaining nitrogen oxide concentrations are below the analyzer’s detection limit) may be provided by zero air in cylinders, zero air generator or adsorbent traps (activated charcoal and Sofnofill© or Hopkalit©).

CALIBRATION STANDARD: at least one NO laboratory standard by a Central Calibration Laboratory should be available at the station, for both annual calibration and the evaluation of working standard drifts.

WORKING STANDARD (NO CALIBRATION): a second certified NO working-standard should be used for routine checks and recalibrations. Commercial NO standard at 5 ppm can be diluted to about 100 ppb by using a dilution unit with mass flow controllers, critical orifices or restrictors. It is recommended that when first attached to the NO standard cylinder, the pressure regulators must be flushed 4-5 times with cylinder air. To avoid atmospheric O₂ from reacting with NO and altering the standard mixing ratio, the regulators should remain under pressure for at least 24 hours and, after again flushing 4-5 times, they are ready for use.

GAS PHASE TRITATION (C_{eff} CALIBRATION): calibration of the photolytic converter for determination of C_{eff} should be carried out at appropriate time intervals. Usually 2-4 days is an appropriate period, since the BLC is usually rather stable. Only at the very beginning of the experimental activity, more frequent checks are recommended due to the faster decrease of the UV lamp emission. For calibration, NO₂ produced by gas-phase titration (GPT) of a NO standard (dilution from 5 ppm to 100 ppb) with added excess ozone (60-70 ppm by UV radiation at 185 nm emitted by Hg lamp) is recommended. The amount of NO₂ generated by GPT can be determined by the decrease in the NO signal on adding the generated O₃.

A detailed procedure for the execution of C_{eff} calibration is reported in GAW (2011). Here, the main points of the procedure are reported:

- i) A known NO mixing ratio is produced by standard dilution and then passed through the darkened BLC or by-passed the BLC: the CLD response to NO is then determined (NO₁).
- ii) The known NO mixing ratio is then passed through the illuminated BLC: this gives the CLD signal due to NO in the standard gas, plus NO from any NO₂ residuals in the standard gas or zero air (NO_{tot1}).
- iii) The O₃ source is activated so that 80% of the known NO mixing ratio is titrated. The extent of titration is determined by the decrease in CLD NO signal with the GPT unit energized and the BLC extinguished or by-passed (NO₂).
- iv) The known NO mixing ratio is again titrated but passed through active BLC and the resulting CLD signal is measured (NO_{tot2}).

The conversion efficiency of the BLC is then calculated from:
$$C_{eff} = 1 - \frac{[NO_{tot1} - NO_{tot2}]}{[NO_1 - NO_2]}$$

3.5 ESTIMATED SET-UP COSTS

The following estimated provisional costs are provided to evaluate the feasibility of WS-CRDS installation at a remote or high-mountain site.

- Instrument cost (Thermo 42iTL): 20.000,00 €
- Blue Light Converter (Droplet Instrument Inc): 6500,00 €
- Zero air generator: 8.000,00 €
- GPT and air dilution system: 15.000,00 €
- NO certified standard gas: 500,00 €

3.6 CONCLUSIONS

With the aim of performing accurate NO and NO_x measurements at high-mountain stations, the implementation of an experimental set-up able to ensure the “Level 2” data quality objective defined by GAW-WMO (2011) is necessary.

To this end, at high-mountain stations where in-situ personnel is not available, “enhanced” (trace level) commercial CLD instruments can be used, in cases when photolytic converter is used instead of “standard” Molybdenum heated converter.

Frequent routine calibration of CLD sensitivity (by challenging the instrument with diluted NO standard gas) and photolytic converter efficiency (by gas phase titration) are mandatory to fulfil the data quality objective. At remote measurement sites, such calibration can be automatized or controlled by remote.

Despite a significant initial financial effort for setting-up the experiment, routine operation appears to be feasible even at remote automated stations. Particular attention should be paid to the evaluation of the power consumption for implementation: CLD analyzer (300 W), GPT system (300 W), Zero air generator (150 W).

3.7 REFERENCES

GAW, Expert Workshop on Global Long-term Measurements of Nitrogen Oxides and Recommendations for GAW Nitrogen Oxides Network, Hohenpeissenberg Meteorological Observatory (Germany, October 2009), 2011.

Steinbacher, M., C. Zellweger, B. Schwarzenbach, S. Bugmann, B. Buchmann, C. Ordóñez, A. S. H. Prevot, and C. Hueglin (2007), Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, *J. Geophys. Res.*, 112, D11307, doi:10.1029/2006JD007971.

4. FEASIBILITY STUDY FOR THE UPGRADE OF THE SAMPLING SYSTEM OF A COMMERCIAL INSTRUMENT FOR THE ON-LINE MONITORING OF PM1 AND PM10

4.1 INTRODUCTION

Observation of aerosol properties, including mass and chemical composition, is one of priorities identified by the GAW-WMO (2007), which stated that “aerosol activities are a core component of GAW because of the importance of aerosols to a wide range of issues including global climate change, weather prediction, and air quality/health.” The GAW aerosol programme objective is “to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality up to multidecadal time scales” (WMO, 2003). In particular, it is recommended to enhance the coverage, effectiveness, and application of long-term aerosol measurements worldwide. The GAW-WMO document emphasized the importance of implementing near-real time data delivery of aerosol information also for “supporting research and development in atmospheric transport and numerical weather prediction models and the production of related products and services”. Finally, GAW/WMO is working to integrate data about mineral aerosol, for enhancing the capabilities of National Hydro-Meteorological Services to monitor and predict sand and dust storms. In particular, total and mass concentration of major chemical components in two size fractions (fine and coarse) are among the five “core” variables indicated by GAW-WMO (2007) for the implementation of long-term aerosol measurements.

For these reasons, in the framework of the NextData project, a feasibility study is currently under way at the “O. Vittori” Station, part of the GAW-WMO Global Station at Monte Cimone. The study concerns the implementation of on-line determination of PM1 and PM10 aerosol mass (with near-real time transmission of recorded data, as well as off-line information on chemical components in the two size fractions).

The present report illustrates the preliminary results of the feasibility study, providing information about the upgrade of the sampling system of a commercial aerosol sampler.

4.2 EXPERIMENTAL SET-UP

In the framework of the upgrading activities carried out at O. Vittori” Station during August 2012, a commercial system (SWAM 5A MONITOR, FAI Instrument S.r.L.) was installed for the on-line monitoring of PM1 and PM10 aerosol fractions. This system determines the aerosol mass using the β attenuation method and is equipped with completely automatic management of sampling and measurement quality controls with immediate validation of the PM_x concentration data. The collected aerosol samples (flow rate of 2.3 m³/h) are stored by the instrument, in order to allow subsequent off-line chemical analyses. The system is characterised by a rather high power consumption (peak value: 1 kW). Thus a careful evaluation of the energy power available at the measurement site was mandatory before installation.

Even if similar systems are already widely used at urban or rural measurement sites, its installation at Mt. Cimone (2165 m a.s.l.) represents, to our knowledge, the first attempt of utilization at a high mountain measurement site characterised by harsh meteorological conditions (high wind speed, frequent summer thunderstorms, winter ice rimming and heavy snow fall).

At the “O. Vittori” Observatory, the system was installed in a laboratory hosting other aerosol samplers (Fig. 4.1). The installation work was rather complex, as the system is designed to work at “air-quality” shelter with a horizontal roof. Thus, several works were carried out, e.g. to adapt the air sampling lines to fit with the station’s slanting roof

4.3 PRELIMINARY RESULTS

The first summer tests revealed episodes of internal instrument flooding, due to the presence of large amounts of water in the sampling heads. These events determined: (i) the stopping of the sampling programme, (ii) the contamination of the collected aerosol samples, and (iii) instrumental damage.

This clearly points to the necessity of upgrading the sampling system in order to function in the challenging weather conditions that can affect high-mountain sites, like Mt. Cimone.

The manufacturer proposed a solution based on the use of a small tank to drain the water from the bottom part of the sampling heads (Fig. 4.2). An automated valve was also inserted at the base of the tank, to allow the drainage of collected water. However, the proposed solution turned out to be not optimal for use at a high-mountain site. In fact, it is evident (Fig. 4.2) that the water tank and valve, embossed to the sampling heads, may represent optimal surfaces for ice riming and wind stress. Moreover, placing the electronically controlled valves outside the laboratory, seriously increases the risks related to lightning or electro-static discharges which sometimes occur at high-mountain sites.

For these reasons, further upgrades were planned and implemented with the aim of adopting non-invasive technical solutions, not based on the use of external devices which could modify the system's sampling efficiency or favour the occurrence of damage due to adverse weather conditions.

Since this kind of instrumentation and sampling systems are rather widespread among SHARE and Italian GAW-WMO Stations, these implementations can be shared with other research groups to improve the accuracy and availability of aerosol information at remote and high-mountain measurement sites.



Figure 4.1. SWAM 5A hosted at the “O. Vittori” Observatory, part of the GAW-WMO Global Station at Monte Cimone.

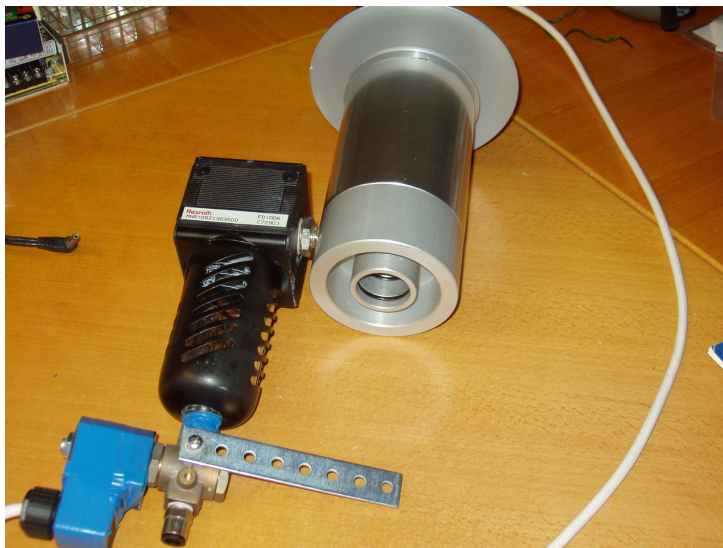


Figure 4.2. Water drainage system implemented by the manufacturer. The black assembly contains the water tank, the blue assembly is the automated valve. It is evident that a similar device is not suitable for use in environment with high wind speed, high possibility of lightning and ice rimming.

4.3.1 Description of implementation

The implementation adopted at Mt. Cimone was based on the use of a cavity present at the bottom part of the sampling heads, created by the manufacturer to reduce the total weight of the system. This cavity was identified for use as the water tank.

The cavity was closed by using a polycarbonate chain ring with watertight o-ring. At radial and central position, a conical hole was dug to accommodate a Tygon® tube (D: 8 mm) for water drainage. The drainage was managed by an automated valve located inside the laboratory. A further hole made in the bottom part of the sampling head allows the drainage of water from the PM10 sampling head to the water tank. For the PM1 sampling heads, which host several stages at the interior, an external by-pass (copper) was installed to allow water drainage (Fig. 4.3).

Both water tanks at the PM1 and PM10 sampling heads were connected to one main drainage line, which was connect to a single automated valve for water drainage. Figure 4.4 presents a technical diagram of the implementation.

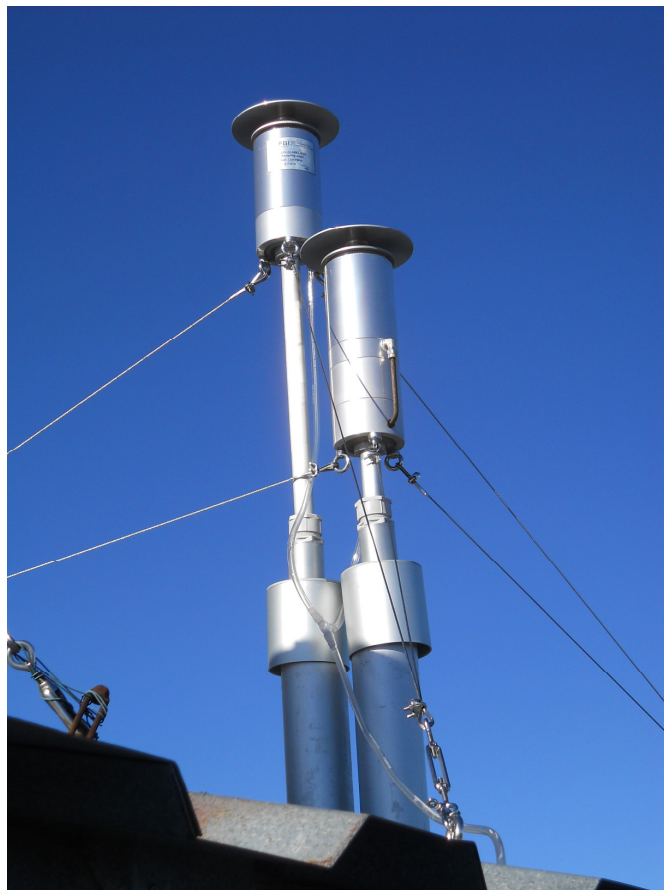


Figure 4.3. Implementation of the new water drainage system. On the right can be seen the PM1 sampling head with the external by-pass for water exchange from the sampling head to the water tank.

4.4 CONCLUSION (PRELIMINARY)

A commercial system (SWAM 5A MONITOR, FAI Instrument S.r.l) has been installed at the “O. Vittori” Observatory, part of the GAW-WMO Global Station at Monte Cimone. This represents a good opportunity for carrying out a feasibility study concerning implementation of on-line PM1/PM10 monitoring at high-mountain stations.

Summer tests showed that the design of the sampling heads was not optimal for working at a high-mountain site: water penetrated into the sampling heads, flooding both the interior of the instrument and the filter stored in the unloaded system. For these reasons, a drainage system was implemented at CNR-ISAC (Bologna Laboratories) to prevent this kind of problem, as well as to avoid possible problems arising from wind stress and ice rimming. After this intervention, no further water floods have been observed. Here, we provided a detailed description (together with technical schemes) of the upgrade.

4.5 REFERENCES

- WMO/GAW Strategic Plan: 2008-2015 - A Contribution to the Implementation of the WMO Strategic Plan: 2008-2011 (WMO TD No. 1384), 108 pp, June 2007
- WMO, Report of the First CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 18-19 March 2003), WMO TD No. 1181, 2003

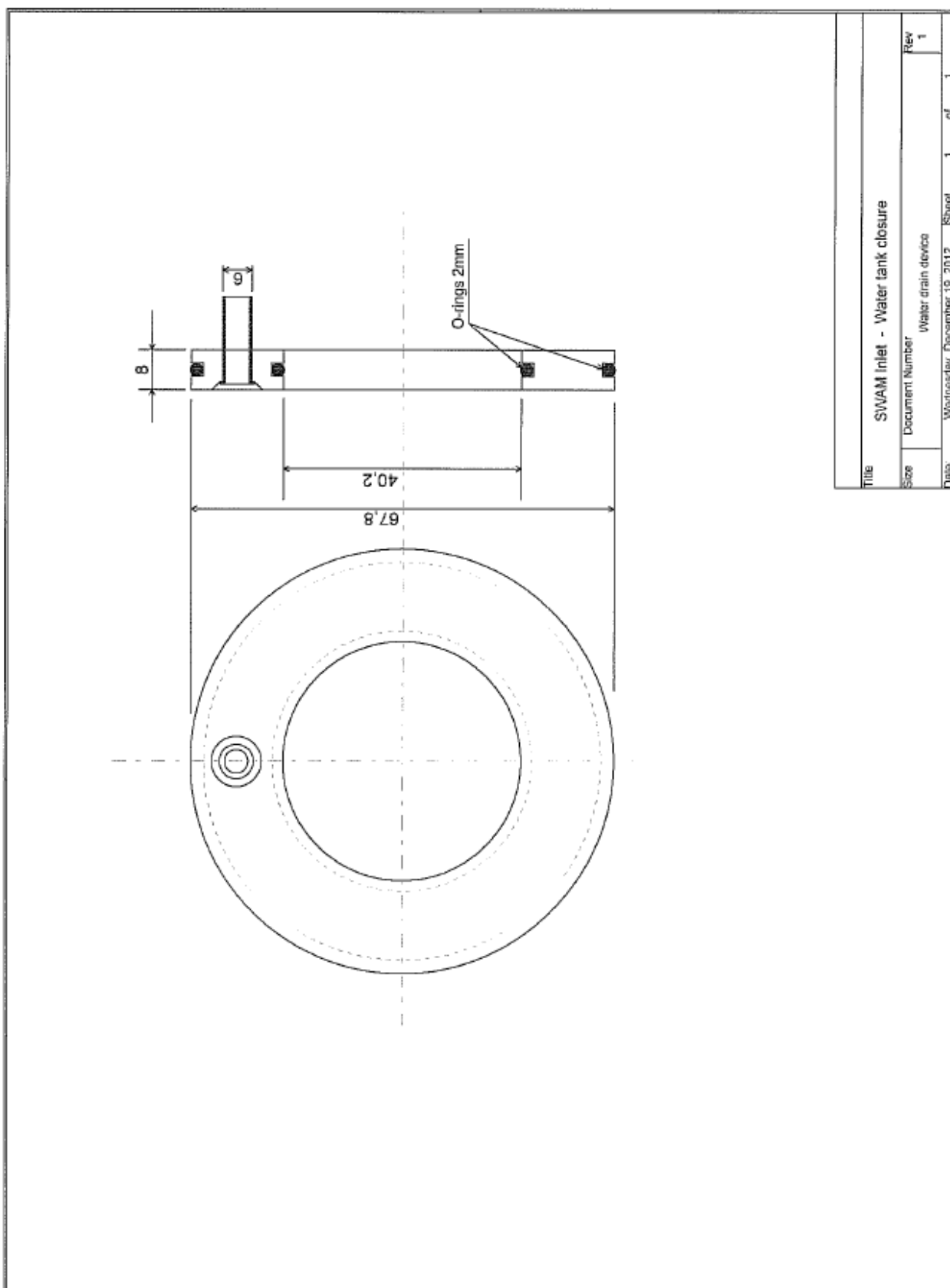


Figure 4.4. Technical scheme showing the design of the feasibility study implementation.

5. FEASIBILITY STUDY FOR THE INSTALLATION OF AN AEROSOL LIDAR AT THE GAW-WMO GLOBAL STATION “O. VITTORI” AT MT. CIMONE

5.1 INTRODUCTION

Aerosols are important constituents of the atmosphere, playing a major role in weather, climate and environmental issues. As reported in the fourth IPCC record (IPCC, 2007), the indirect and direct effects of aerosols largely contribute to the total uncertainty of radiative forcing. As indicated by the GAW (2008), observations of vertical aerosol field are mandatory to improve the understating of aerosol processes and their implications on the aforementioned issues. In particular, information relating to vertical aerosol distribution is extremely important for a better assessment of aerosol-climate interaction, because most effects of aerosols on climate occur at elevated layers. At the same time, the implementation of aerosol vertical distribution measurements is important also for air-quality issues focusing especially on investigating the role of transport and transformation processes occurring at different spatial scales.

Until now, no continuous observations of aerosol vertical profiles have been carried out at the GAW-WMO Global Station at Mt. Cimone, part of the NextData Project. As reported in the GAW-WMO Strategic Plan 2008 – 2015 (GAW, 2007), "to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality up to multidecadal time scales" is a primary goal. To this end, the GAW Atmospheric Lidar Observation Network (GALION) was launched with the objective of "providing the vertical component of this (aerosol) distribution through advanced laser remote sensing in a network of ground-based stations" (Task. 7.84 of the GAW-WMO Strategic Plan 2008 - 2015).

In particular, the aerosol properties to be observed include:

- 1) aerosol layers, profiles of optical properties with known and specified precision (backscatter and extinction coefficients at selected wavelengths, lidar ratio, Ångström coefficients),
- 2) aerosol type (e.g. dust, maritime, fire smoke, urban haze) and microphysical properties (e.g., volume and surface concentrations, size distribution parameters, refractive index).

It is clearly indicated that "observations should be made with sufficient coverage, resolution, and accuracy to establish comprehensive aerosol climatology, to evaluate model performance, to assist and complement space-borne observations, and to provide input to forecast models of chemical weather".

Thus, the implementation of continuous aerosol LIDAR observations at the GAW-WMO Global Station at Mt. Cimone is a key-activity for responding to the GAW strategy. Moreover, the implementation of such an experimental programme at this GAW-WMO Global Station will provide information about the presence, altitude and extent of elevated aerosol layers, mixing layer height, aerosol typology and mass concentration. This will significantly upgrade the capacity of interpreting the variability of the other key-compounds (greenhouse and reactive gases, in-situ aerosol chemical-physical properties) already observed at the station.

The present work describes the results arising from a study undertaken at the "O. Vittori" Station (part of the GAW-WMO Global Station of Mt. Cimone) during 2012, for evaluating the feasibility of installing a LIDAR system. This is a mandatory activity for accurately evaluating the criticalities related to the

installation of similar advanced instrumentation in remote high-mountain sites, where usually no personnel is present in-situ and where the environmental and logistic complexities can be severe.

The report is organized as follow. First, a description of the experimental set-up is provided. Then, the results of the feasibility study are presented and discussed. Finally, recommendations for future implementation are made.

5.2 EXPERIMENTAL SET-UP

The LIDAR used in this feasibility study is similar to those deployed at the CNR base of San Pietro Capofiume (SPC, in the Po Valley) and at the AWI Arctic research station at Ny Aalesund (Svalbard), and is the result of collaboration between CNR and ENEA (Figure 5.1).

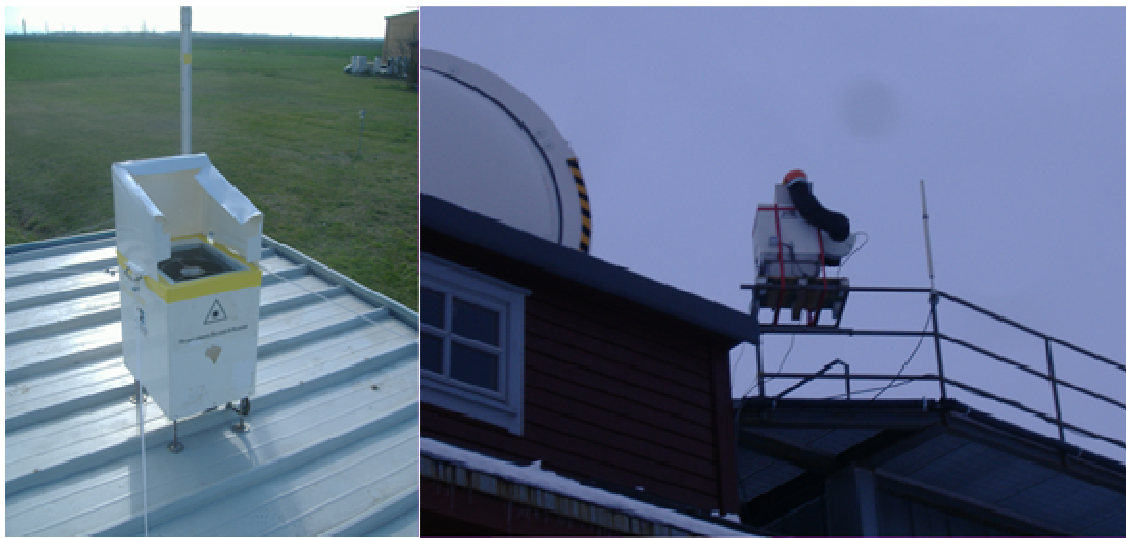


Figure 5.1. The LIDAR system installed on the roof of a container at the experimental base of San Pietro Capofiume (left panel) and on the roof of the AWI station in Ny Aalesund (right panel).

It is a **backscatter (BL) depolarization lidar (DL)** with **night-time Raman capabilities (RL)**. A synopsis of the system specifications is given in Table 5.1. The aerosol parameters retrievable from the system are:

- Range corrected signal (colour plots of aerosol and cloud distributions)
- Attenuated backscatter coefficient (calibrated range-corrected signal)
- PBL depth
- Aerosol backscatter coefficient
- Aerosol type discrimination (dust, anthropogenic)
- Aerosol extinction coefficient (estimate), optical depth, column lidar ratio

5.2.1 System description

The opto-electronic system of the LIDAR is housed within an aluminium box electronically shielded and thermally insulated with polyurethane. The temperature in the box is controlled by four cooler-heater Peltier cells, 20W each, and by an additional 100 W heater, which maintain the temperature inside in the range required by the laser operating conditions. The laser is a diode pumped Nd-YAG (manufactured by Bright Solutions), with second-harmonic generation and active Q switching. The laser pulse duration is 1 ns and the emission is on two wavelengths, with energies of $350 \mu\text{J}$ / pulse at

532 nm (green) and 800 μ J / pulse at 1064 nm (near infrared). The pulse repetition rate is 1 kHz. The system is air cooled and has a power consumption of less than 250W (10A @ 24V).

From factory specifications, the laser beam divergence is 3 mrad and is further reduced by a factor of 7 by a beam expander. The half divergence sddiv has been tested in the field, proving to be different along the two main directions of the cross section of the beam. This leads to a decrease in the energy density across the beam cross section that declines with distance from the emitter, rendering the beam eye safe at 1500 m from the instrument.

The laser beam is sent into the atmosphere via a steerable mirror placed before the beam expander, which allows fine alignments of the beam.

Parameter	Specifications
Detected Wavelengths	1064, 608 and 532 nm (Pol resolved)
Laser Type	Nd-YAG (1064 and 532 nm)
Pulse duration	1 ns
Laser repetition rate	up to -1 kHz
Laser output energy	0.8 mJ at 1064 nm; 0.35 mJ at 532 nm
Telescope diameter	20 cm
Telescope type	F/1.5 Newtonian
Telescope field of view	0.7 mrad
Beam divergence	0.4 mrad, full angle x 7 expanded
Filter Bandwidth	2 nm
Vertical Resolution	From 7.5 to 150 in photoncounting mode; From 1.875 to 15 m in current mode.
Vertical range	1024 x Vertical Resolution
Time resolution	down to 1s

Table 5.1 Technical specifications of the LIDAR system.

The optical receiver of the LIDAR is composed of a Newtonian telescope with a diameter of 20 cm, f/1.5, with a field of view of 0.7 mrad regulated by a field stop of 200 microns. A grey photochromic glass is placed in the focal plane of the telescope to reduce the efficiency of the system by a factor of 4, under conditions of strong sky background light, thereby reducing the effects of saturation in the signal detection. The backscattered light is collimated and divided by spectrally low-pass dichroic cubes, and then filtered by narrow band interference filters with bandwidth of 2 nm (Semrock) to separate the backscatter at 532, at 608 (Raman nitrogen used - only in nighttime conditions - for absolute calibration of the system) and 1064 nanometers. A cube polarizer is used to further subdivide the radiation at 532 nm in the components polarized parallel and cross to the laser radiation emitted. The radiation at 608 and 532 nanometers is focused on miniature photomultiplier modules (Hamamatsu 5783P and 6780-20 respectively) with very low thermal noise (less than 10 counts / s at 25 ° C). The 1064 nm radiation is focused into an Avalanche Photo Diode (APD) C30954E (EG&G) with 0.8 mm photo sensitive area diameter.

- In current mode, the electrical signal from the photomultiplier is filtered through a 15 MHz low pass, to avoid aliasing effects, and then digitally recorded and converted into a digital 8 bits waveform. The duration of a single sampling time can be adjusted to the values of 12.5, 25 50 or 100 ns, for a total of 1024 samples. The different settings provide a reconstruction of the

vertical profile, in current mode, with a resolution of 1.875, 3.75, 7.5 and 15 m for a vertical extension of 1.85, 3.75, 7 and 15 km, respectively (the first 24 samples are prior to the laser shot and are used to measure the sky background signal).

- In photon-counting mode, the electrical impulses originating from a single photon detection, are discriminated at an adjustable threshold level to reject spurious noise, forming TTL pulses which are then counted in 1024 consecutive time windows of adjustable length from 25 to 1000 ns in 25 ns increments. This allows the reconstruction of a vertical profile extending at least 7.5 km and at most 150 km, this length being adjustable in 7.5 km steps. Similarly, the vertical resolution can be adapted from 7.5 m up to 150 m, in 7.5 m steps.

5.2.2 Acquisition system

The acquisition card provides the average of the signals averaged over N laser shots. Thus, profiles are produced as means over an average time that can range from 1 s (i.e. a minimum of 1000 laser shots, whereas the frequency of repetition of the shot amounts to 1 kHz) to tens of hours. The averaging time can be adjusted via software. A satisfactory compromise between good signal statistics and a sufficient temporal resolution is obtained by setting the time average between 5 to 30 s. Such average profiles are stored in the memory board of the system (500 MB, expansible to several GB), which allows the accumulation of tens of thousands of profiles. An external computer is used to access the system, and a dedicated software package sets the parameters of the acquisition card (the average duration to create the profile, the vertical extension of the profile and its resolution, the frequency and power of the laser pulse and so on) via USB connection.

The system starts data storage when it is turned on, and stops when it is turned off, or whenever an appropriate command is sent from an external computer, as, for instance, when it is necessary to stop the data storage to download the data. Data files are stored as ASCII files. Each file reports information on the system settings and raw data (series of photon-counts/s, or averaged waveform digital units).

A customized software is available for producing the geophysical parameters of interest (backscatter coefficient and depolarization profiles) from the raw data. A real time visualization of the measurements is possible on an external computer via a suitable software package, for system checking purposes or alignment.

5.3 RESULTS

The LIDAR system was installed at the “O. Vittori” Station on 23 October, 2012. It was located on the equipped terrace of the laboratory. The system was connected to the power and data lines of the station. This allows for the remote control of the system and near-real time data download. Even if the system was already operative just after the installation, the beginning of experimental activity had to be postponed until 16 November, 2012 due to the delay in obtaining the permit to operate (NOTAM) from the National Aviation Authorities.

5.3.1 Study of system sensitivity to sunlight

The photon-counting mode technique, preferable in the acquisition of atmospheric returns from distant ranges, due to the better signal to noise ratio, tends to become saturated in bright daylight. In such conditions, the current mode is viable. A region of overlap exists between current and photon-counting mode recordings, allowing a merging of the two modes of acquisition to reconstruct the whole backscattering profile from a few meters from the instrument to the maximum altitude of the sounding. The region where the two acquisition modes coexist, is generally identified between 2 km

and the top of the analog profile, 3.75 km or higher. In this region, the photon-counting mode still has a good linearity and the current mode is still sensitive enough. In the region of partial overlap between the laser beam and the FOV of the telescope, the atmospheric signal is reconstructed using the procedure described in Biavati et al. (2011), thus extending a reliable atmospheric profile down to only 100 m from the instrument.

A study was performed to test the sensitivity of the system in daylight conditions, which appear to be the most burdensome for this measurement technique. The results are shown in Figure 5.2, where two curves indicate the values of the aerosol backscatter coefficient with a signal to noise ratio equals to 1, as a function of the distance from the instrument (range). The black and red curves refer to 5s, and 60 s integration time, respectively.

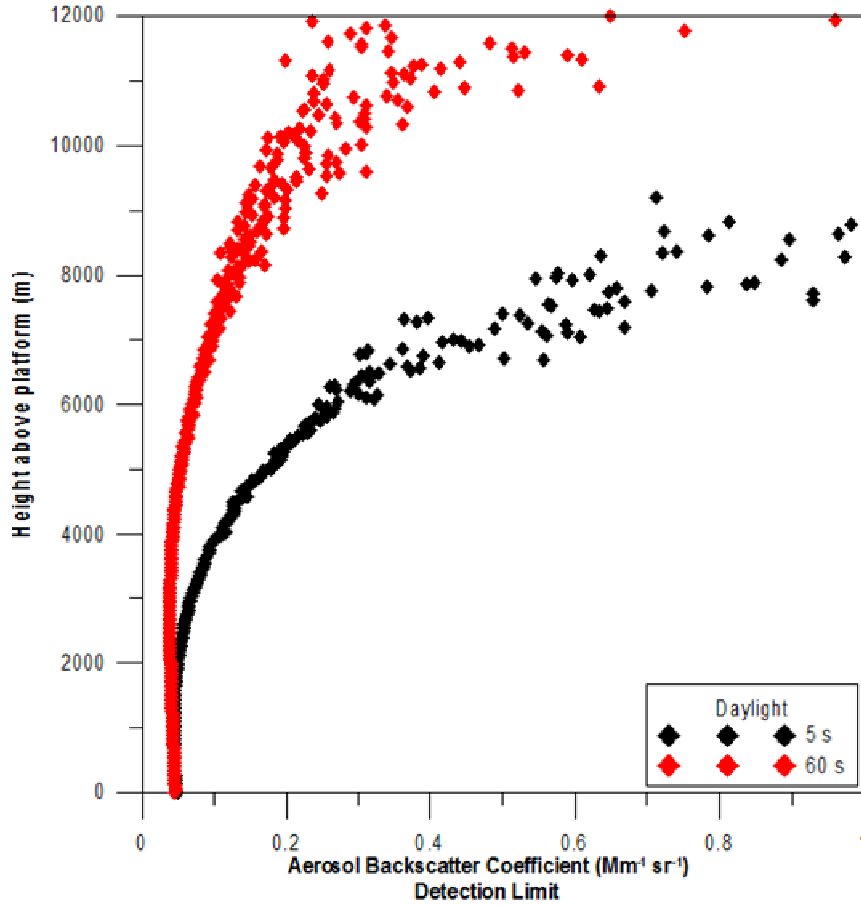


Figure 5.2. Graphs of the minimum detectable aerosol backscatter coefficient (in the worse conditions of sky background light) as a function of altitude, for 5s and 60s of integration time.

5.3.2 Performance evaluation

Some preliminary results are presented, relating to the data obtained during the installation of the LIDAR system in Monte Cimone station. Figure 5.3 reports the background subtracted, range corrected signal for one 30 s average single profile, (red line for the polarized channel, black line for the depolarized channel), while Figure 5.4 reports a one-day time series, the colour coding the background subtracted, range corrected signal from the polarized channel. It clearly illustrates the evolution of the tropospheric aerosol content, as well as some thick clouds at 6 km (first part of the day) and at 10 km (second part of the day) where the colour code saturates to white.

Starting on 4, December 2012, despite the correct functioning of the system (as deduced by the analysis of internal parameters), no more good data were obtained in terms of aerosol profiling. As suggested by the inspection of real-time meteorological data and as subsequently confirmed by a technical survey (Fig 5.5), the system was completely covered by ice rims and snow accumulation. Although an external blower with a laminar diffuser continuously cleans the glass window at the top of the system (already successfully operated at Arctic locations, see Di Liberto et al, 2012), it clearly appeared to be ineffective for the hard meteorological conditions which can characterise Mt. Cimone.

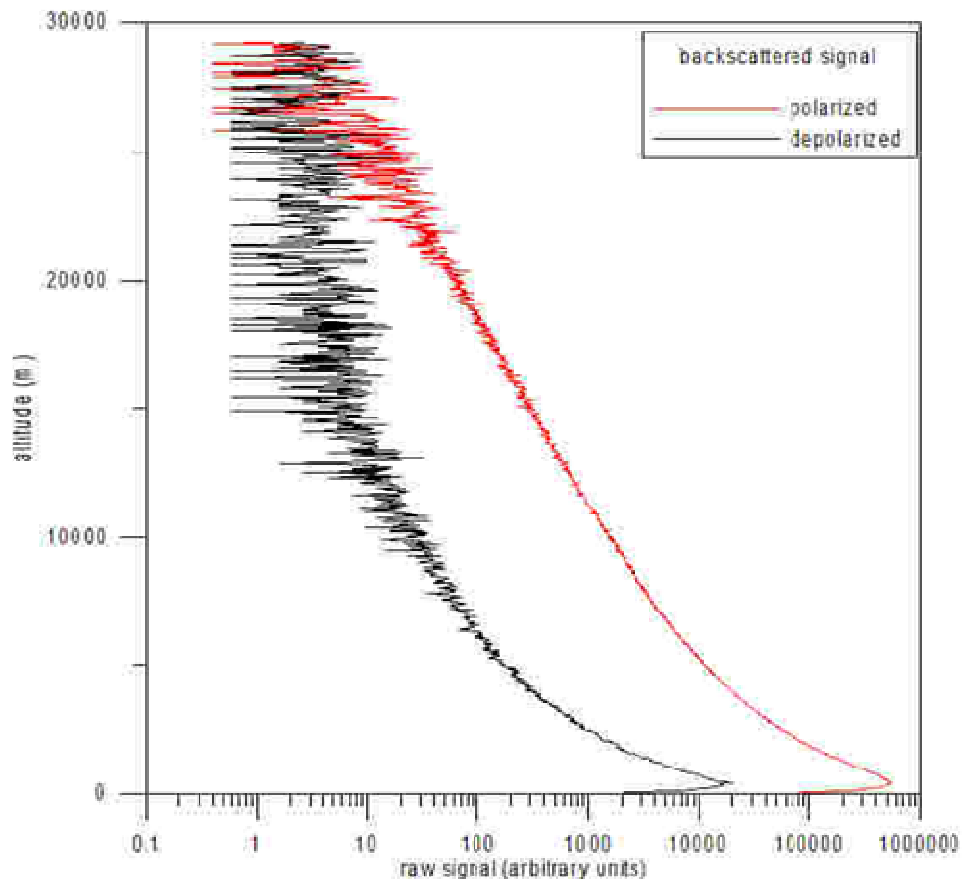


Figure 5.3. Background subtracted range corrected signal from the polarized (red line) and depolarized (black line) channel, from a 30 s measurement session, vs altitude. Data were acquired on 17 November at 4:35 LT. The atmosphere shows virtually no notable aerosol/cloud relevant features. The depolarization channel is able to profile up to 10 km, the polarization channel up to 30 km.

As shown by the time series of meteorological parameters continuously collected at the “O. Vittori” Station, starting from 28 November 2011, very humid air-masses (RH ~100%) continuously affected the measurement site with air-temperature below freezing point. This is a rather common occurrence at Mt. Cimone, especially when south-western flow (transporting humid air-masses from the near Tyrrhenian Sea) affect the measurement site, as in this case (Fig. 5.6). A further indirect indication of severe air formation at the measurement site is provided by the interruption of wind direction data (due to ice rimming of the sonic wind sensor, despite the presence of an enhanced de-icing system), precisely when the recorded air-temperature dropped below 0°C on 28 November, 2012.

As revealed by the time series of the internal parameters recorded by the acquisition system, even in these hard conditions the components of the LIDAR system worked properly, and the only reason for the observation failure can be attributed to the ineffectiveness of the external cleansing device for these very extreme meteorological conditions. This indicates that the LIDAR system tested at Mt. Cimone and its single components (transmitter, receiver, data acquisition) are characterised by an objective robustness for operation in adverse meteorological conditions. However, to assure wide data coverage and high data quality, outdoor installation of the system is not feasible unless a robust cleansing system is installed.

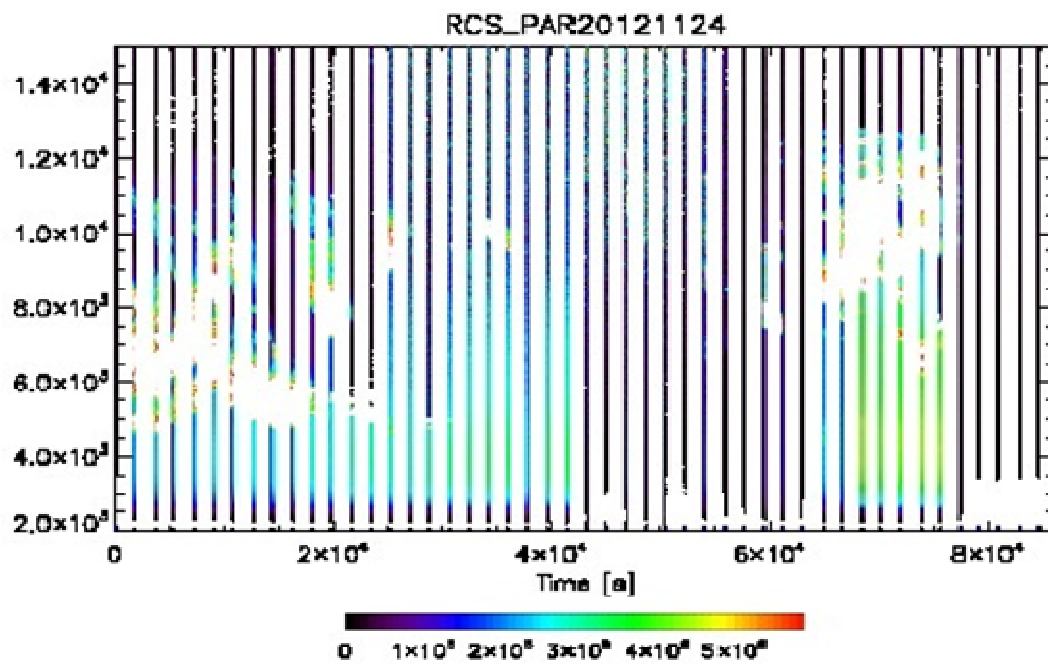


Figure 5.4. Colour coded time series of background subtracted range corrected signal from the polarized channel, from subsequent 30 s measurement sessions, vs altitude. The evolution of the atmospheric aerosol content can be traced during the day.



Figure 5.5 External view of the LIDAR system on 5 December, 2012, as encountered during the technical survey.

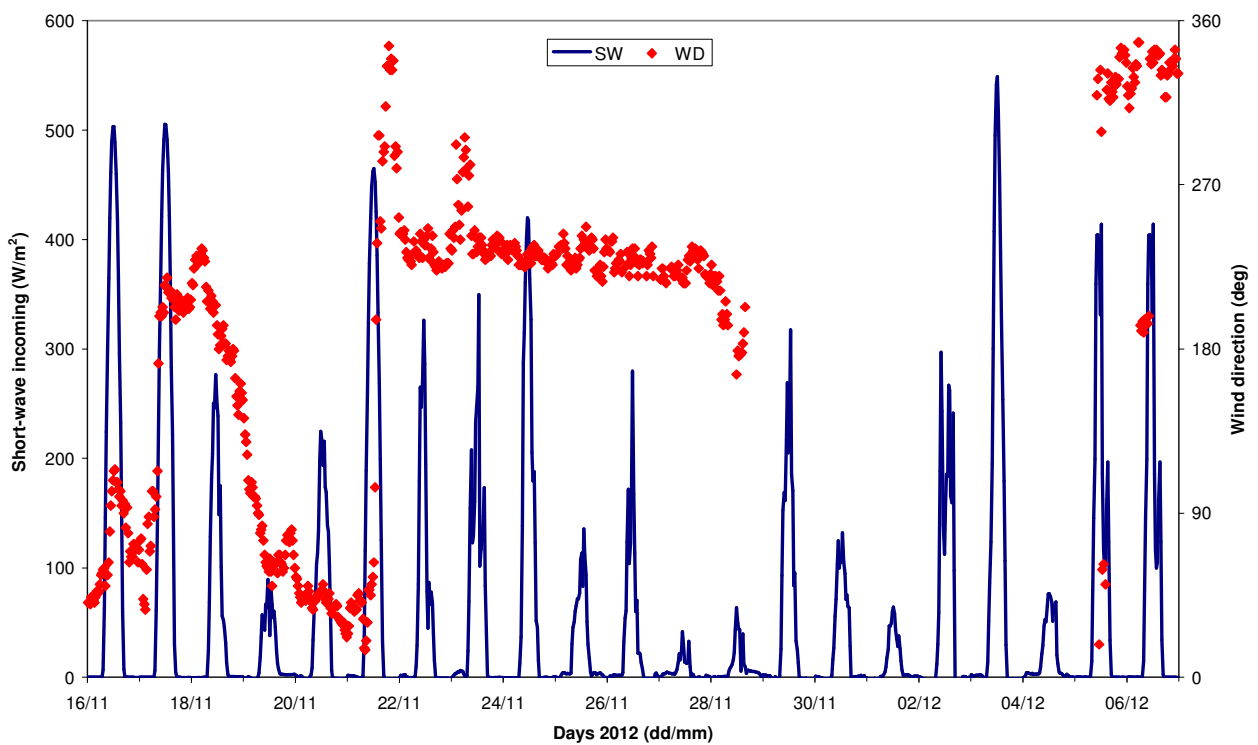
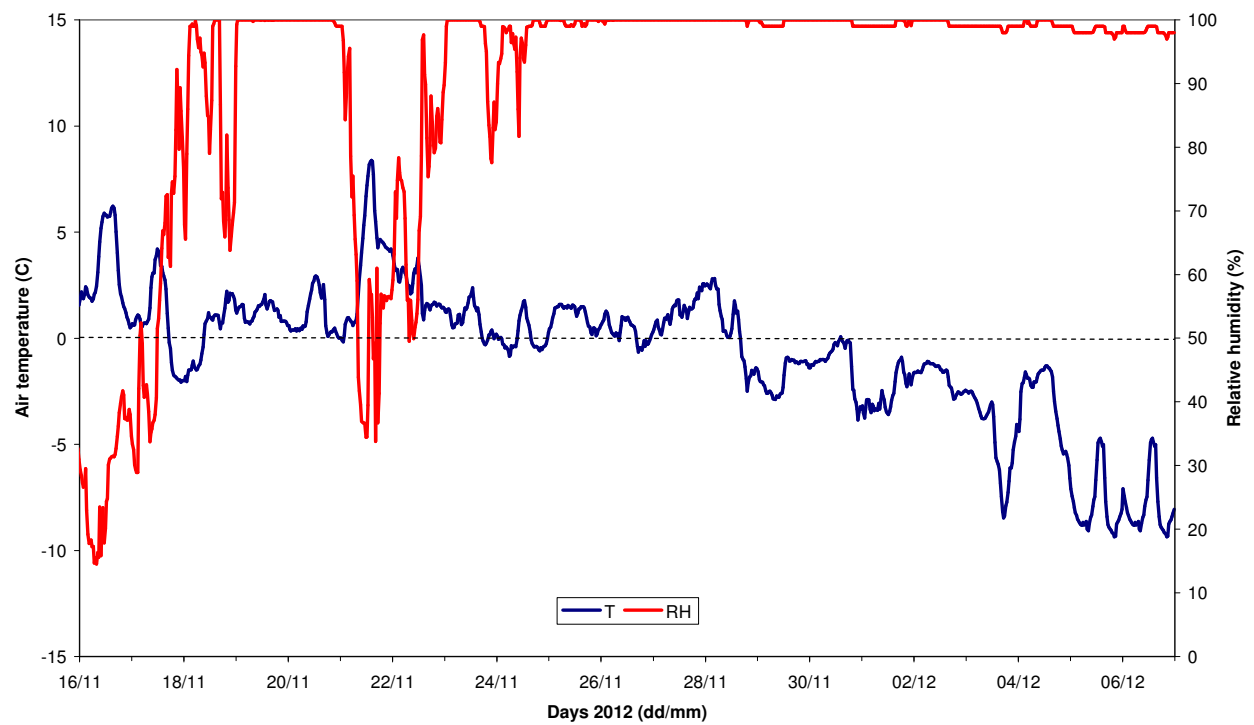


Figure 5.6. 30-min average values of air-temperature, relative humidity (upper plate) and wind direction and incoming solar radiation (bottom plates) from 16 November to 6 December 2012.

5.4 CONCLUSIONS

Based on the results of the feasibility study, the LIDAR developed at the CNR-ISAC laboratory in Rome, appears to be suitable for installation in remote observatories where no continuous presence of personnel is possible.

The results of the study also indicate that, due to the very adverse meteorological conditions that can affect Mt. Cimone, it is necessary to deploy the system in the interior of the station. At this stage, no laboratories are ready to host this kind of equipment which, for instance, requires specifically designed roof-window. For this purpose, further investigations are necessary to identify the possible infrastructural upgrades for allowing the continuous functioning of a similar system at the “O. Vittori” Observatory.

Special attention should be deserved for in-situ operation, since the laser beam is not eye safe.

5.5 REFERENCES

- Cairo, F., Di Donfrancesco, G., Di Liberto, L., and Viterbini, M.: The RAMNI airborne lidar for cloud and aerosol research, *Atmos. Meas. Tech.*, 5, 1779-1792, doi:10.5194/amt-5-1779-2012, 2012.
- Di Liberto, L., Angelini, F., Pietroni, I., Cairo, F., DiDonfrancesco, G., Viola, A., Argentini, S., Fierli, F., Gobbi, G., Maturilli, M., Neuber, R., and Snels, M.,: Estimate of the Arctic Convective Boundary Layer Height from Lidar Observations: A Case Study, *Ad. Met.*, 1–9, 851927, doi:10.1155/2012/851927, 2012.
- Biavati G., Di Donfrancesco G., Cairo F., and Feist D. F.: Correction scheme for close-range lidar returns *Applied Optics*, Vol. 50, Issue 30, pp. 5872-5882 <http://dx.doi.org/10.1364/AO.50.005872>, 2011.
- IPCC, Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, 104 pp, 2007.
- GAW, Plan for the implementation of the GAW Aerosol Lidar Observation Network GALION (Hamburg, Germany, 27-29 March 2007) (WMO TD No. 1443), 52 pp, November 2008.
- WMO/GAW Strategic Plan: 2008-2015 - A Contribution to the Implementation of the WMO Strategic Plan: 2008-2011 (WMO TD No. 1384), 108 pp, July 2007.