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TABLE OF CONTENTS

1 Executive Summary

Introduction

Ozone in the earth's upper atmosphere absorbs ultraviolet radiation, preventing most of it reaching the ground. This is important because ultraviolet radiation can harm life on earth, and for example lead to skin cancer. Since the 1980s, it has been known that human-produced chlorofluorocarbons (CFCs) have led to recurring losses of total ozone in the Antarctic (the ozone hole), and these have also been recently observed in the Arctic, while in middle-latitudes, moderate ozone depletion has been observed.

The Montreal Protocol on Substances that Deplete the Ozone Layer is an international treaty signed in 1994 designed to protect the ozone layer by phasing out the production of substances that are responsible for ozone depletion, and it has been successful in reducing the emission of ozone-depleting substances.

However, monitoring of the recovery of the ozone layer requires accurate long-term observations with reliable and well understood instruments and the development of future instrumentation.

This project characterised key reference and network instruments for the traceability of ozone retrievals (or measurements), developed new instruments and devices for in-field characterisation of the existing network instruments and new ozone monitoring instruments, and generated new datasets for ozone absorption cross sections and extra-terrestrial solar reference spectrum.

The Problem

Atmospheric ozone has been defined an Essential Climate Variable in the Global Climate Observing System (GCOS) of the World Meteorological Organisation (WMO). This means that it is considered to critically contribute to the characterisation of the earth's climate. Careful long-term monitoring of the global ozone layer from the ground and from space is crucial in verifying the successful implementation of the Montreal Protocol, and its anticipated eventual recovery to pre-1970s levels.

CFCs were once widely used in insulating foam and aerosol spray-cans. Once released, they gradually spread through the atmosphere, eventually reaching the ozone layer which lies within the stratosphere around 25 km above the ground. Once there, they destroy the ozone. CFCs have now been almost completely replaced by chemicals that do not cause this damage.

Nevertheless, recovery of the ozone layer has not been observed so far, and model projections have shown that the recovery will not take place before the middle of the 21st century. There is a need for instruments giving measurements that enable us to reliably monitor and record the predicted worldwide recovery of the ozone layer.

The Solution

This project has made significant improvements in explaining substantial differences and quantifying the corresponding uncertainties of worldwide monitoring total column ozone (TOC) from the Earth's surfaces with different instrument types and leads, therefore, to a homogenisation of ozone monitoring data products. Furthermore, the project provides the technical and research fundament of replacing ageing instruments with more cost effective, robust and accurate instrumentations of newest generation for detecting of the recovery of the world-wide ozone shield during the next decades.

Impact

The project results represent important improvements towards more reliable measurements of total column ozone and the harmonisation of global ozone monitoring networks:

- The importance and impact of well characterized Dobson and Brewer instruments has been demonstrated to the TOC monitoring community in two field campaigns, two stakeholder workshops and trainings. In addition to the laboratory-based methods for the characterisation and calibration of the network instruments, the project can now provide to the end-user also methods and devices for in-field characterisations and calibrations.
- The new extra-terrestrial spectrum displays a traceable benchmark dataset for traceable spectral solar irradiance, with low and known uncertainty.

- The overall uncertainties of ground-based ozone monitoring are now well quantified. A software tool is available to assess the overall uncertainty of ozone measurements by different network instruments.
- A current European Horizon 2020 research program providing a “Virtual Observatory” for essential climate variables including total column ozone has now a tool to homogenize the different ground based ozone networks with well quantified uncertainties
- The technical developments of the project prepared the development of potential new generation of cost effective, robust and reliable instruments for monitoring ozone with requested uncertainty for the next decades.

2 Project context, rationale and objectives

Context

Since the 1980’s, it is known that human-produced chlorofluorocarbons (CFCs) have led to recurring massive losses of total ozone in the Antarctic (ozone hole), which have also been recently observed in the Arctic, while in middle-latitudes, moderate ozone depletion has been observed. The Montreal protocol and its amendments have been successful in reducing the emission of ozone-depleting substances. Nevertheless, a recovery of the ozone layer has not been observed so far, and model projections have shown the recovery to occur not before the middle of the 21st century. Atmospheric ozone has been defined as an essential climate variable (ECV) in the Global Climate Observing System (GCOS) of the World Meteorological Organization (WMO). Careful long-term monitoring of the global ozone layer is still crucial in verifying the successful implementation of the Montreal Protocol and its amendments on the protection of the ozone layer, with the eventual recovery of the ozone layer to pre-1970’s levels. Currently, the European Horizon 2020 research program for the Gap Analysis for Integrated Atmospheric ECV Climate Monitoring (GAIA-CLIM) is on progress to improve, homogenize and providing traceability and uncertainty of ground based observations of essential climate variables – including total column ozone - in a “Virtual Observatory”. This project is essential to monitor the successful implementations of the Montreal protocol and to support the global “Virtual Observatory” with traceable ground based observations of ozone.

Rationales

To address the challenges of the context, the project had to characterize key reference and network instruments for traceability of ozone retrievals, to developed new instruments and devices for field characterisation and future new ozone monitoring instrumentations and to successfully generate new datasets for ozone absorption cross sections and extra-terrestrial solar reference spectrum.

The most reliable total column ozone measurements are obtained from UV spectroradiometers, measuring the differential absorption of ozone in direct solar irradiance measurements. Two instruments, the Dobson and Brewer spectrophotometers, are responsible for the most extensive ground-based measurements producing benchmark datasets used to infer the long-term evolution of the ozone layer. The Dobson spectrophotometer network has the most extensive dataset, starting in 1926, while the Brewer spectrophotometer started measurements in the early 1980’s. Even though each network-type is in itself consistent, total column ozone retrieved from the two instrument types differ by up to 3%, which is significantly larger than the consistency of better than ±0.5% which can be achieved within Brewer or Dobson instruments. Therefore, this large discrepancy currently precluded a merging and homogenisation of both datasets and an eventual replacement of one instrument with another type such as array spectroradiometers.

The work within the project was to define common parameters to use, so that total ozone retrievals remain consistent among each instrument group. This included also the generation of new data sets of ozone absorption cross sections and an extra-terrestrial solar reference spectrum, with state-of-the-art measurement techniques with known uncertainties. Furthermore, the discrepancies between different instrument types prevent the phase-out or replacement of the ageing Dobson spectrophotometer with newer instruments since it would represent a break in the long time-series of ozone measurements and make it more difficult to detect ozone recovery.

There was therefore a need for an improved characterisation and calibration of the Dobson and Brewer instruments, particularly by involving the reference instruments of each network. This thorough characterisation has now an impact on the whole global observing network by disseminating improved ozone measurements with known uncertainties. The characterizations as well as the definition of common parameters (including the new datasets) investigated in this project prepared the way of the development of an eventual replacement of the traditional Dobson spectroradiometers which require substantial manpower to operate (manual operation of the instrument) and are not being manufactured anymore. Due to the results of the scientific and technical research, cost effective and robust array spectroradiometers are the most promising instrumentations to fulfil the overall objective of homogenizing past and future ozone monitoring time series with traceable and reduced uncertainties.

Scientific and technical objectives

Objective 1: Characterization of Dobson and Brewer reference instruments order to ensure a consistency between the individual network instruments and within the two networks:

- Characterizing the spectral bandwidth and wavelength of the World Reference and European Reference Dobson spectrophotometers (and 2 standard network instruments) in the range 300 nm to 350 nm.
- Characterizing the spectral bandwidth, wavelength, out-of-range stray light and temperature of several Brewer spectrophotometers.

Objective 2: Development new devices for measurements and characterization of the Dobsons, Brewer and full spectrum instruments such as array spectroradiometers with following devices:

- A field-suitable tuneable radiation source (TuPS) in the UV range for the bandwidth and wavelength characterisation of Dobson spectrophotometers with a wavelength uncertainty of 0.05.
- A field-suitable wavelength ruler to characterize and calibrate the wavelength of Brewer and array spectroradiometer instruments.
- A field-suitable UV-LED light source to track the stability of array spectroradiometers.
- A dedicated high-resolution array spectroradiometer system (ERMIS) for direct spectral solar UV irradiance measurements in the range 300 nm to at least 350 nm.

Objective 3: Generation of new reference data sets:

- Improved ozone absorption cross-section data in the Huggins-band, with known uncertainties
- A benchmark high resolution extra-terrestrial solar spectrum in the wavelength range 310 nm to 350 nm with the uncertainties.

Objective 4: Overall uncertainty budget of ozone retrieval.

- Develop uncertainty models for correlated quantities with application to the total column ozone retrieval for Brewer, Dobsons and full-spectrum instruments.
- Determine a comprehensive uncertainty budget for Dobson, Brewer, and array spectroradiometers.

Objective 5: Ozone intercomparison campaign

- Organise and participate at two international field campaigns with the characterised reference Brewer and Dobson spectrophotometers in addition to newly available array spectroradiometer systems (Pandora, Phaethon, Ermis) in order to validate and assess the total column ozone retrieval and respective uncertainties.

3 Research results

3.1 Characterization of Dobson and Brewer reference instruments

Why characterization of Dobson and Brewer instruments: The Dobson and the Brewer spectrophotometers are the primary ground-based instruments used to report total ozone column (TOC), which is obtained from the differential absorption of select wavelengths in the UVB part of the solar spectrum. However, ozone measurements from Dobson and Brewer instruments network have shown systematic discrepancies of up to 3%, which is significantly larger than can be achieved within Brewer and Dobson instruments. These discrepancies have been partly traced back to uncharacterized instrumental features. Therefore, the characterization of the Dobson and Brewer instruments will result in reducing the discrepancies between the two networks.

3.1.1 Dobson Characterisation

Dobson spectrophotometer was the first instrument type developed for measuring the atmospheric ozone layer. A global network of Dobson instruments for ground-based monitoring of Total Ozone Column (TOC) has been established and has been in operation since several decades. The Dobson TOC-retrieval algorithm requires widths and center wavelengths of the bandpass functions of the spectrophotometers. The bandpass functions of every individual instrument are not known. They are assumed to be equal to those of the world reference Dobson. Therefore, the assumption of a standard bandpass function and the deviation from the real bandpass may cause substantial differences in the TOC measurement.

The consistency among the network instruments is ensured based on well-defined assembly and operating procedures as well as on field comparisons against the reference Dobsons. However, some systematic discrepancies in the results of individual Dobsons and between Dobson and Brewer instruments have been observed. The discrepancies have been partly traced back to uncharacterised instrumental features. Hence, a direct optical characterisation of the instruments shall offer a metrological basis for the TOC measurements helping to understand and to decrease the discrepancies.

The aim of the project was to characterise several reference instruments from the TOC network of the Dobson spectrophotometers by using the metrological facilities and expertise of the NMIs project partners. Moreover, it was also aimed to develop and provide to the TOC monitoring community a portable instrument, which could enable in-field characterisations of the network Dobsons with respect to their bandpass and wavelength properties.

PTB, together with an external collaborator, Deutscher Wetterdienst (DWD), developed procedures for the characterisation of Dobsons instruments using its pulsed wavelength-tuneable laser facilities while CMI, in close interaction with CMI, has applied its reference monochromator setup for the same purpose. PTB characterised the world reference Dobson No. 083, the European regional reference Dobson No. 064, and two network Dobson instruments: No. 101 (Swiss) and No. 013 (Portuguese). CMI characterised the second European reference Dobson No. 74. While the world reference Dobson No. 83 already had a data set from the bandpass measurements back in the 90’s, the characterisation of the other Dobsons was carried out for the very first time in their usage history. Thus, altogether 5 Dobson spectrophotometers were characterised at the highest metrological level in the framework of the project. The results (see Figures 3.1.1.1-.2) revealed that the characteristics of the regularly serviced instruments are alike, which is obviously due to the well-established optical alignment procedures for the Dobson instruments. From the 5 instruments characterised in the NMI laboratories, only one network instrument, No. 101, had its optical alignment not up-to-date, which presumably was the reason behind a somewhat larger deviation as compared to the other instruments that had been serviced within a short time frame before the characterisations.

The second important finding beyond the state of the art was, that the bandpass functions of the instruments deviate from the nominal ones used with the TOC algorithm (see Figure 3.1.1.2). Using the determined bandpass functions and the new absorption cross-sections of ozone (IUP), the so-called effective absorption coefficients for use with the TOC derivation algorithm could be calculated. It was shown within the Izaña intercomparison campaign that such data does improve the consistency of the Dobson data and ideally would be available for every network instrument.

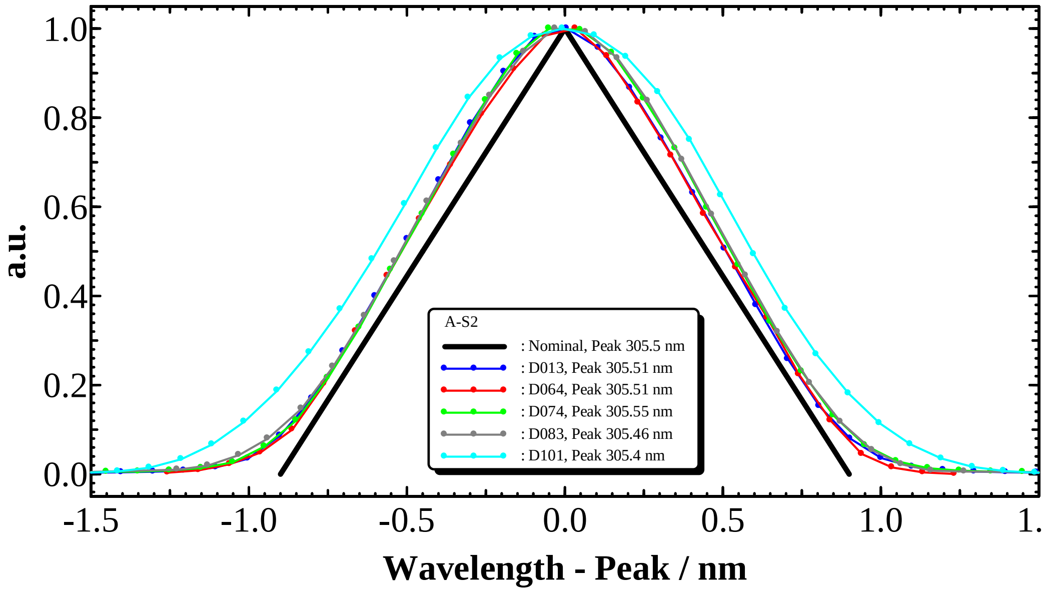


Figure 3.1.1.1. Nominal and measured bandpass functions for the A-S2 slit of 5 Dobson instruments. The wavelengths are shown relative to the peak values.

The portable tuneable radiation source (TuPs) developed by CMI for in-field characterisation of the Dobsons was successfully tested during a regional Dobson intercomparison at Hohenpeißenberg in Germany in June 2017 (see section 3.2.1). The TuPs instrument was used to characterise the participating Dobson spectrophotometers. It provided data consistent with that from the laboratory measurements and was well accepted by the end-user community as a highly-needed instrument. Thus, the developed tool could be regularly used during Dobson calibration campaigns to improve the network homogenisation.

Active collaboration and synergy among the task partners was the key components to the success of the Dobson characterisations within the project. The NMI partners (CMI, PTB) brought in their metrological competence while the non-NMI partners (DWD, CMI, REG (ULL)) the know-how of the instruments and the procedures for the TOC retrieval.

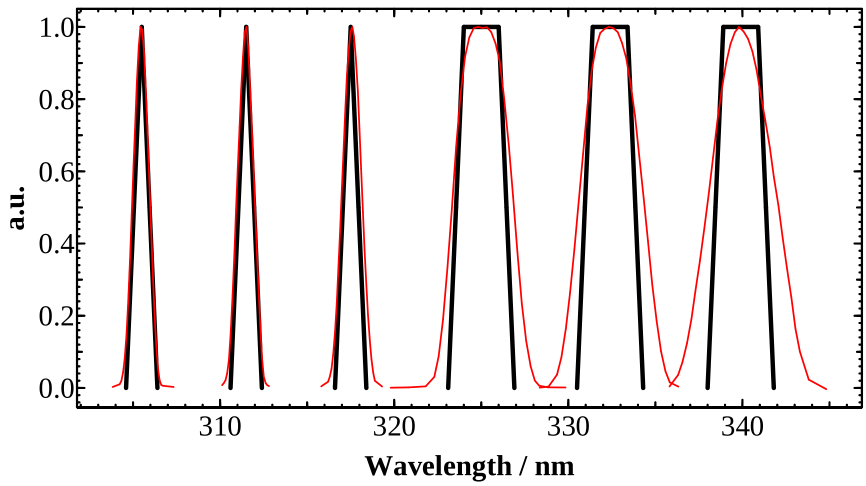


Figure 3.1.1.2. Nominal (thick black lines) and measured (thin red lines) bandpass functions of the world reference Dobson No. 83.

3.1.2 Brewer Characterisation

In analogy to the Dobson characterisation, reference instruments from the Brewer network had to be characterised in terms of wavelength and bandwidth. Additionally, the Brewer instruments were characterised for temperature dependency, out of range stray light and filter behaviour.

Temperature characterisation

To make a thorough study of the effect of temperature on Brewer measurements, a characterisation of the temperature dependence in two experiments were conducted in the PTB (March 2016, February 2017, see Figure 3.1.2.1) and Kipp (October 2016) facilities to validate the standard methods for the determination of the temperature dependence of the Brewer measurements used to retrieve atmospheric TOC. This work allows to compare the measurements made through the different input ports of the instrument, the effect of temperature on the Brewer observations modes O3, UV and AOD and the implications of this on measurements. It also allows to compare and validate the temperature correction coefficients obtained in the laboratory and those obtained using the current standard procedure in EUBREWNET, which uses field data of the Brewer standard lamp. While the temperature effect over the global UV measurements of the Brewer spectrophotometer has been studied by different authors, so far no validation of the temperature sensitivity of the ozone retrieved from Brewer has been reported.

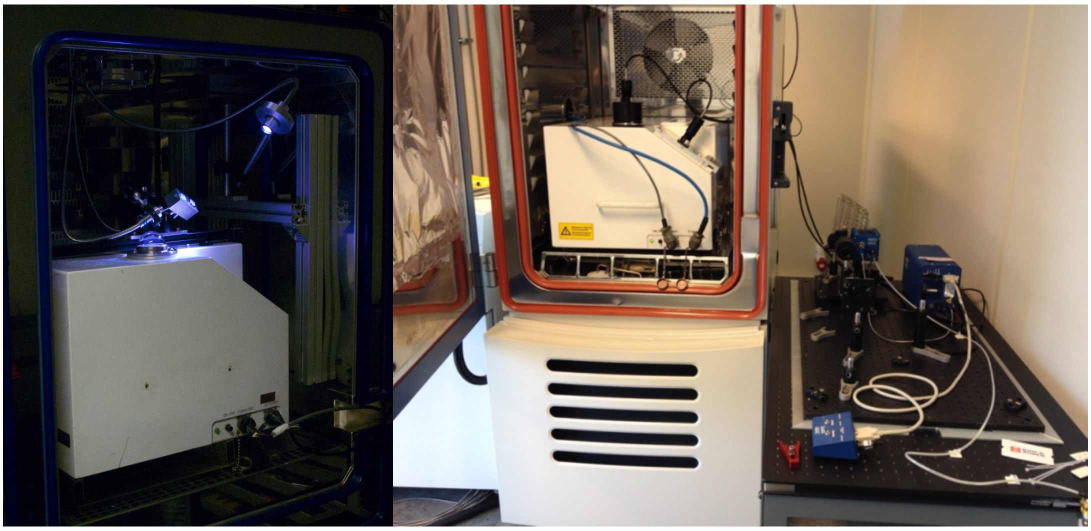


Figure 3.1.2.1. Experimental setup showing the Controlled Temperature Chambers used at the PTB facilities (left) and at the Kipp facilities (right).

The experiments show some unexpected results, the temperature dependence of the absolute measurements does not show on most of the cases the linear dependence and the measurements using the direct port shows a remarkable hysteresis.

Concerning the ozone calculation which use relative coefficients determined lead to differences of the TOC below of 0.5%. This is so even though the values of the relative coefficients obtained by the different types of used lamps, and therefore different spectral irradiances, present wide differences. This is possible because the algorithm used to retrieve TOC remove any linear effect with the wavelength, and the wavelength selection for the ozone calculation of the Brewer spectrophotometer is made to guarantee this condition.

While the behaviour of the relative measurements are approximately linear with temperature, absolute measures generally exhibit behaviours that may become difficult to model. This implies that the temperature coefficients used in the determination of TOC should not be directly used to correct the temperature sensitivity of AOD or UV Brewer measurements, which should be analysed separately.
The difficulty of obtaining absolute coefficients from the measurements in the thermal chamber is probably due to the way the temperature changes affects to the different elements in the Brewer spectrophotometer. Dilations in the fore optics affect the alignment of the system causing a proportional change in all

wavelengths. The effect on the monochromator causes small changes in the wavelength. Finally the temperature affects the photomultiplier causing a nonlinear response mainly at high temperatures.

Finally, it is worth to note that temperature correction is usually applied to experimental measurements using a reference temperature close to the most frequent operation temperature. But this is not the case with the Brewer spectrophotometer, which use a reference temperature of 0°C while the mean operation temperature is 23°C and a median value of 22°C. A change of the reference temperature will reduce the error associated with the uncertainty of the temperature dependence calculation.

Wavelength and Bandwidth characterisation

The Brewer instrument can operate both as spectroradiometer, i.e. scanning over a range of wavelengths, and as ozone spectrophotometer, i.e. measuring ratio of signals at different fixed wavelengths without scanning the monochromator. The wavelength and bandpass calibrations of the instruments is performed in the first mode while the results are extrapolated to the second mode. Wavelength and bandpass characterisation of the instrument in the ozone mode would require sweeping the wavelength of a narrow-band source. This was realised within project in a collaboration between PTB and REG(ULL). Respective procedures were developed that enabled to carry out such measurements by using a wavelength-tuneable laser source (see Figures 3.1.2.1). One of the European reference Brewer instruments and two other Brewers were characterised this way.

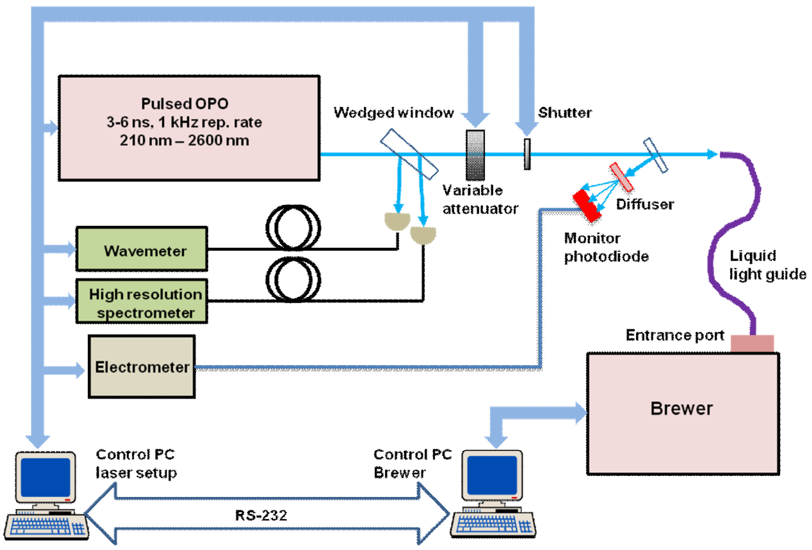


Figure 3.1.2.2. Setup at PTB used to measure bandpass functions and peak wavelengths of Brewer spectrophotometers.

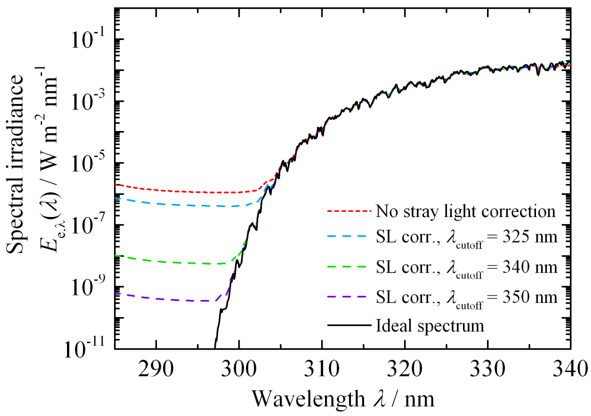
The results for the characterised reference Brewer showed the bandpass functions to be triangular instead of commonly used trapezoidal parametrisation. Another result obtained from the dispersion measurements for this instrument was that the normally used quadratic fit to the wavelength approximation is not sufficient. A cubic polynomial fit utilising more reference wavelength points could improve the accuracy of the dispersion correction.

Out-of-range stray light

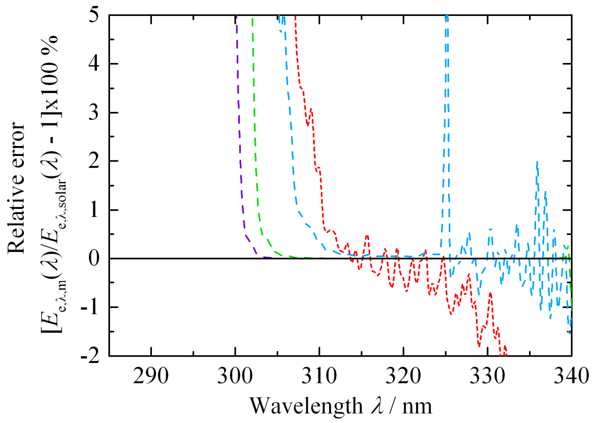
Single-monochromator Brewer spectrophotometers suffer from stray light-caused errors, especially at short UV wavelengths where the solar irradiance level drops rapidly with decreasing wavelength. Consequently, stray light also affects ozone retrievals. To decrease such errors, special bandpass filters are used with their transmission band limited to the measurement range of the instrument – which for Brewer MKII instruments extends nominally to 325 nm – which should prevent generation of stray light by radiation outside the measurement range of the instrument. Despite of such hardware-based precautions, stray light effects have still been observed in the Brewer results. One of the objectives of the project was to verify whether the observed stray light effects could have been caused by insufficient blocking properties of the filters, i.e., by the out-of-range stray light. To our knowledge, the out-of-range stray light properties of Brewer spectrophotometers have not been studied directly before.

To study the out-of-range performance of single-monochromator Brewer instruments, Aalto and PTB characterised Brewer MKII instruments of Finnish Meteorological Institute (FMI) and Deutscher Wetterdienst (DWD), respectively, using laser-based setups. No stray light above the noise-floor of the measurement was observed at laser wavelengths higher than about 340 nm in either of the characterizations. However, some wavelength dependent differences in the shape of the line spread functions were observed at in-range excitation wavelengths in the measurements of PTB.

To quantify how stray light affects solar UV measurements and ozone retrievals, simulations of stray light contribution from different wavelength regions were carried out, based on the measurement results. The results of the simulation are shown in 3.1.2.4. The results indicate that significant part of the stray light is left uncorrected if the correction is carried out only up to the nominal edge of the measurement range of the instrument, 325 nm. The situation is significantly improved if the correction can be extended to 340 nm. The simulated relative errors in total ozone column, calculated directly from the spectra using the Brewer retrieval method, were -1.6 %, -0.3 %, and -0.004 % for the case where no correction is applied, and for stray light corrections up to 325 nm and 340 nm, respectively. Therefore, it is recommended that stray light from wavelengths between 325 nm and 340 nm is accounted for in one way or another when measuring with a single-monochromator Brewer.



(a)



(b)

Figure 3.1.2.4. Simulated effect of stray light in Brewer MKII instruments and stray light corrections carried up to a wavelength of λ_{cutoff} on the solar UV measurement at a solar zenith angle of 75°, as (a) spectral irradiance, and (b) as relative error to the ideal spectrum.

Filter characterisation

Solar blind filters are used in single-monochromator Brewer instruments to reduce out-of-range stray light. They consist of a nickel sulfate ($NiSO_4$) element sandwiched between UG-11 glass filters. One new filter (provided by Kipp) and three used filters (provided by Kipp and AEMET) were characterized for spectral and spatial transmittance. No leaks above the noise-floor of the measurement – between 10^{-7} and 10^{-6} – were observed for wavelengths longer than 360 nm, see Figure 3.1.2.5 a. The new filter had relatively good spatial uniformity apart from one spot towards the edge of the filter where the transmittance dropped by about 10 %. One of the old filters was spatially uniform, while severe spatial no uniformities were observed for two of the old filters, see Figure 3.1.2.5 b. The standard deviations of spatial transmittances in the centre regions ranged from 0.17 % to 14 % between the filters. The spatial no uniformity is likely to be caused by deviations in $NiSO_4$ density, and can potentially lead to issues, e.g., if the spot where the radiation hits the filter changes between measurements due to poor mechanical repeatability of the monochromator.

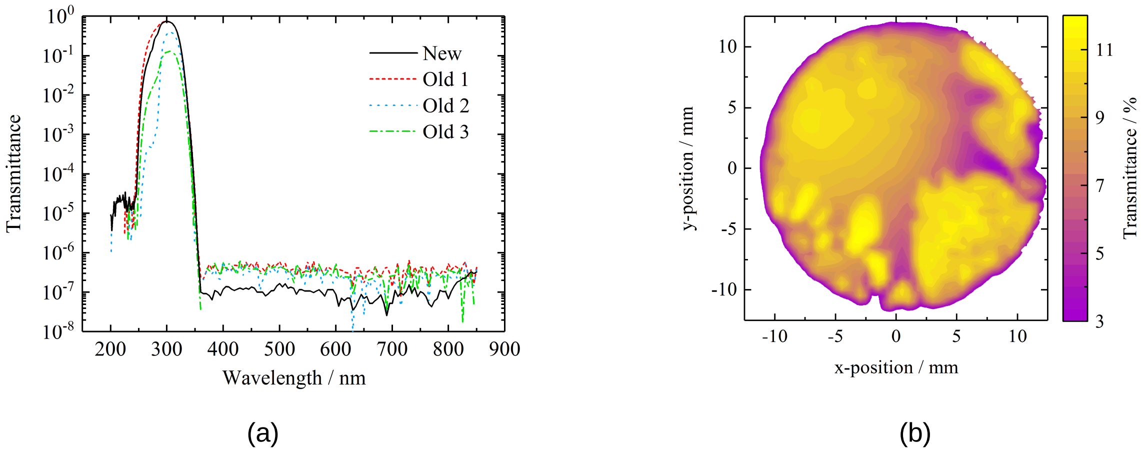


Figure 3.1.2.5.: (a) Spectral transmittances of the solar blind filters studied. (b) Spatial transmittance of the filter 'old 2' measured at the radiation wavelength of 325 nm.

Summary: The objective of characterizing the Dobson and Brewer reference and network instruments in order to ensure a consistency between the network instruments and the two networks themselves has been fully achieved: The measured bandwidth of the Dobson instruments led to a consistent retrieval of total column ozone within the Dobson network. The thorough characterisation of the Brewer reference instruments led to the metrology based conclusion that the used bandwidth is consistent, the operational temperature correction can be applied and that a stray light correction for single Brewers needs to be considered.

3.2 Development of new devices for characterization and measurement

Why new devices for measurement and characterisations: The research undertaken for objective 1 and described in section 3.1 showed clearly the importance of characterising Dobson, Brewer and array spectroradiometers. However, the aforementioned characterisations were provided with devices available in laboratories at National Metrology Institutes. In order to characterise the entire instrument network in-situ at the corresponding ozone observation sites, field suitable devices have to be developed. This section presents these characterisation devices.

3.2.1 Characterisation Devices

Portable tuneable radiation source

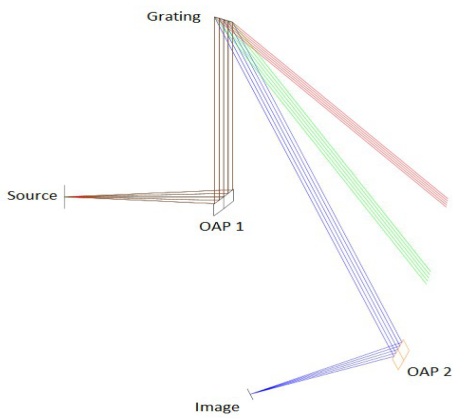
The Dobson instrument evaluates TOC via measuring the ratio of solar radiation intensities between defined wavelength pairs in the spectral range 300-340 nm and calculating a convolution of the instrument slit function (traditionally taken from the handbook specification), laboratory-derived ozone cross-sections and extra-terrestrial constants (ETCs) derived using the Langley plot technique. The original assumption, that all Dobsons would have the identical optical parameters with the published specification was not confirmed experimentally (see section 3.1.1). Therefore, the use of effective ozone absorption coefficients (EACs) convolving the ozone cross-section with the real measured slit functions for each individual Dobson spectrometer should improve the Dobson data quality and its comparison with the modern Brewer spectrophotometer, where these EACs have already been applied.

The Tuneable Portable UV Radiation Source (TuPS) aims to allow providing fast in-field accurate characterisation of Dobson spectrometer slit function and wavelength scale with accuracy as high as they were achieved by the PTB and CMI reference laboratory-based instruments described in section 3.1.1. It is worth to note these laboratory based characterisation techniques requested transportation of Dobson to and from the calibrating laboratories and included time demanding adaptation of existing reference facilities at the laboratory, which result in approximately one day measurement time per one Dobson instrument. TuPS, when applied in situ at the place of international calibration campaigns, can characterise and derive the EACs for each participating Dobson in expected measuring time of one hour.

Design of the device: To be able to provide accurate characterisation of Dobson spectrometers, TuPS should achieve following critical parameters: spectral range between 290 nm to 345 nm, emitted radiation bandwidth narrower than 0.1 nm (FWHM), wavelength scale uncertainty 0.05 nm, minimal spectral radiant power 20 nW (this value was experimentally established during the lab-based characterisation of Dobson #074 in CMI in 2016).

Initial design of the TuPS was based on application of fibre coupled accordion gratings developed by CSEM Neuchâtel, Switzerland. These MEMS elements were promising solution mainly due to their potential robustness and high optical throughput. Although intended MEMS double accordion grating system achieved requested parameters in NIR and IR spectral range, first experiments revealed insufficient optical throughput and wider bandwidth in UV spectral range. Further investigation showed that the limits are connected with the MEMS construction and couldn't be easily and efficiently overcome for intended application. As an alternative solution CMI started developing optical system grating based on the combination of off-axis paraboloid reflection mirrors (OAP) and diffraction grating. Beside the demanding optical parameters mentioned above the optical set-up was aimed to be preferably compact and small in the size enabling its portability.

First design works were focussed on Zemax ® modelling and ray tracing performed for four different optical layouts. This study resulted in choosing the V-shaped optical layout combining two identical OAPs and flat holographic reflection grating. The model predicted feasibility of all desired spectral parameters and optical throughput as high as 28 % for this optical layout. First laboratory-based prototype experimentally confirmed all modelled parameters (see Figure. 3.2.1.1).



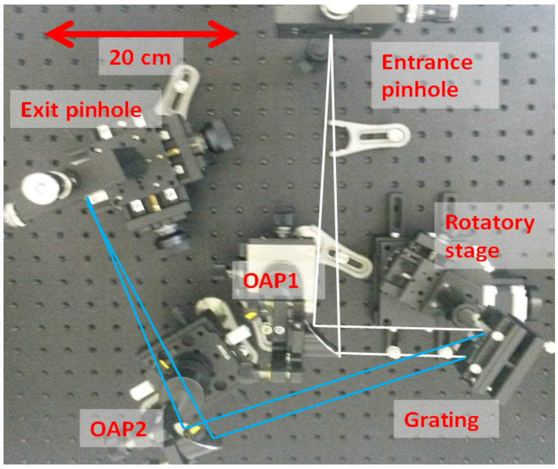


Figure 3.2.1.1: Schematic diagram of TuPS V-shaped optical layout (left) and photo of laboratory-based first prototype of TuPS (right)

Following to these experiments CMI has developed the second prototype (3.2.1.2 and 3.2.1.3). It contains high-grade opto-mechanical components, light-tight cover and home-made optical bench providing both mechanical and optical link between TuPS and Dobson spectrometer. Compared to the first prototype it has been optimised for minimal size too. Systems operation as well as whole Dobson characterisation process is controlled and fully automated by in CMI developed Lab-view software.

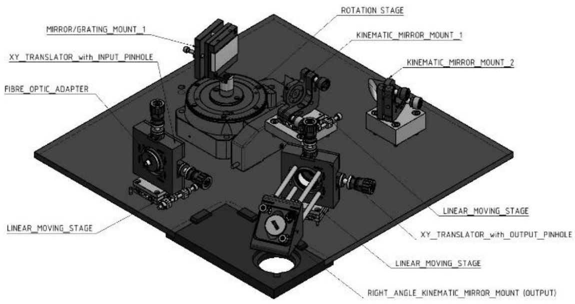


Figure 3.2.1.2: 2nd prototype of TuPS

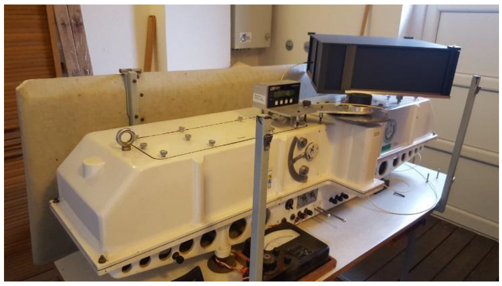


Figure 3.2.1.3: First TuPS measurements of Dobson spectrometer

Wavelength scale uncertainty, optical throughput and spectral bandwidth laboratory characterisation: The TuPS wavelength scale calibration, i.e. the determination of the relation between the grating rotation angle and the selected wavelength at the output, and spectral bandwidth measurement were provided in CMI using the fibre coupled reference tuneable Optical Parametric Oscillator laser facility (OPO). The wavelength of OPO laser pulses was monitored by CMI reference wave meter with the accuracy lower than 0.02 nm. The power of radiation emitted from the TuPS optical output was measured by a calibrated Si photodiode in conjunction with a calibrated trans- impedance amplifier. Same setup was used for measurements of spectral bandwidth. In order to have enough optical power at the TuPS output slit to be detected with a sufficient signal to noise ratio by the Dobson instrument an optical fibre coupled high intensity broadband Laser Driven Light Source (LDLS) was used as input radiation source. Using the same measurement setup used for the TuPS wavelength calibration described above it was also measured the optical power from 300nm to 350 nm.

The results of both the short- and long-term stability of TuPS wavelength scale calibration are presented in Figure 3.2.1.4. It proves that the TuPS wavelength scale uncertainty 0.03 nm all over spectral range of interest significantly within required value. The results of optical throughput and spectral bandwidth measurements. It shows spectral radiant flux exceeding desired minimum value of 20 nW over all spectral range. Measured bandwidth 0.12 nm slight exceeds requested value of 0.1 nm.

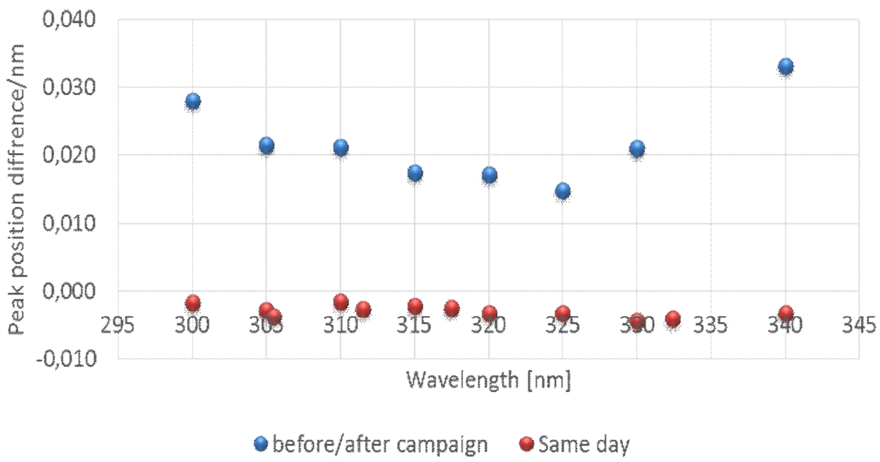


Figure 3.2.1.4: Results of measurements of short and long-term stability of TuPS wavelength scale Temporal stability of TuPS wavelength calibration was tested in two modes: (a) repeating the wavelength calibration before and after running set of measurements during the day in the laboratory during one day – red dots, (b) repeating the calibration before and after the transportation to CMII Hradec Kralove and performing infield measurement (worst case) – blue dots

Between June and September 2017 TuPS characterised a group of 12 Dobson spectrometers: one instrument in CMI Hradec Kralove (Czech Republic) and 11 instruments at Dobson campaigns in Hohenpeissenberg (Germany) and Huelva (Spain).
The results showed a good agreement to the laboratory measurements and led to a comprehensive slit function analysis of the participating instruments.

The project partners with strong support from the project collaborators successfully developed a tuneable portable UV radiation source for in-field characterisation of Dobson spectrometers slit function and wavelength scale –TuPS. The performance of the new device is equivalent as time consuming laboratory measurements also undertaken within the project. The new device allows deriving the effective ozone absorption coefficients (EACs) of each individual Dobson spectrometer directly on its measuring sites or at the site of international comparison campaigns. Measuring time needed for characterisation of one Dobson spectrometer is typically 1 hour. The end-user community showed strong interest in in using this device at the standard Dobson intercomparisons. The National Metrology Institutes will provide characterisation services for the Dobson community with the developed instrument or even create a plan for commercialisation if more devices are needed.

Wavelength ruler

Spectroradiometers, measuring spectral radiance or irradiance, require calibration of their wavelength scale. In the UV part of the spectrum there are no many reference lines available and they are not equally distributed in the spectral range of interest. Additionally, they can consist of multiplets or they can be of low intensity. Finally, not all the wavelength standards can be conveniently used for on-site calibrations. VSL has realised a wavelength ruler for wavelength scale calibration in the range 290 – 350 nm (Figure 3.2.1.5).

This device essentially consists of a properly designed spectral filter which provides a regular interference-like pattern. If such pattern is stable enough and known, it can be used to determine the accuracy of the wavelength scale of an instrument of interest. A typical measurement consists of, at least, three measurement steps:

1) a dark measurement, with no input signal offered to the spectroradiometer.
2) a measurement with the light coming from a broad-band source directly measured by the spectroradiometer to be calibrated
3) a measurement where the wavelength ruler is inserted between the light source and the spectroradiometer.

By taking the ration between the dark-measurement corrected data from step 3 and step 2, one is essentially left with the reference spectrum of the wavelength ruler which can then be used to determine the wavelength scale of the instrument of interest (Figure 3.2.1.6).

In our case, the light source used to perform the measurements is a Light-Driven Light Source (LDLS) Energetiq EQ-99, arranged in a way to produce a collimated beam of radius of about 20 mm diameter. A long pass filter at 280 nm has also been placed on the beam path, in order to prevent radiation below that wavelength from reaching the instruments.

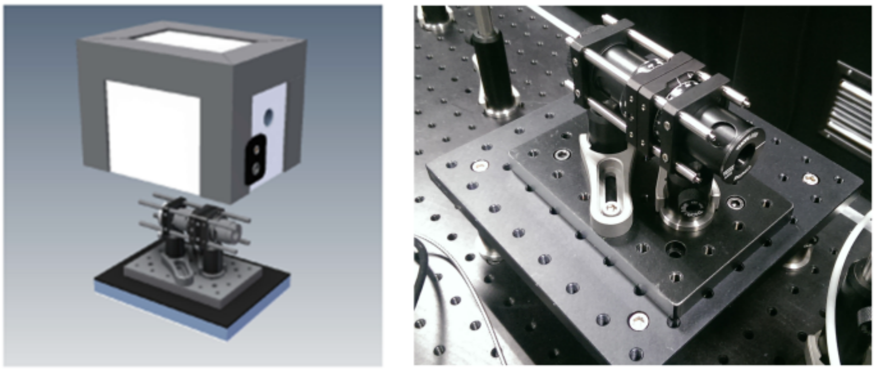


Figure 3.2.1.5: A view of the wavelength ruler in all its main components (left) and a detail on the actual realisation for the optical components (right).

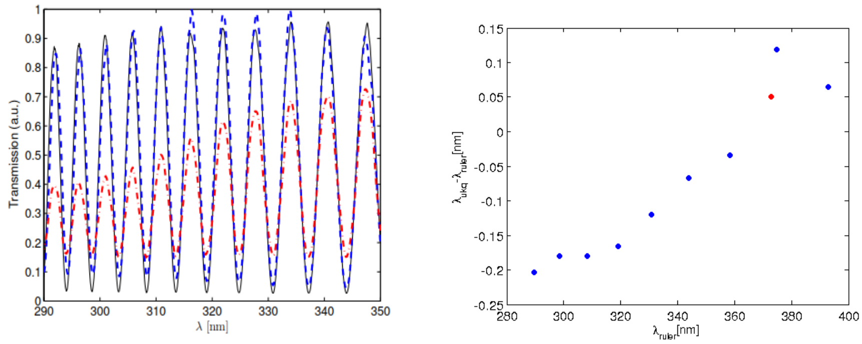


Figure 3.2.1.6: Spectral response wavelength ruler as measured by three diﬀerent systems. Left: Transmission as measured by three different systems. The red curve has been measured by a double-monochromator system available at VSL. The blue and black curves have been measured by two array spectrometers produced by two different manufacturers. Right: difference between reference wavelength and wavelength scale of an array spectrometer. The rod dot in that panel represents the measured wavelength of a reference laser line at 372 nm.

In September 2016 a three-week measurement campaign has been organized at the Centro de Investigación Atmosférica de Izaña, Tenerife, Spain. During the measurement campaign of Izaña, different types of instruments have been measured and under different measurement conditions. Fig. 3.2.1.7 shows the measurements results.

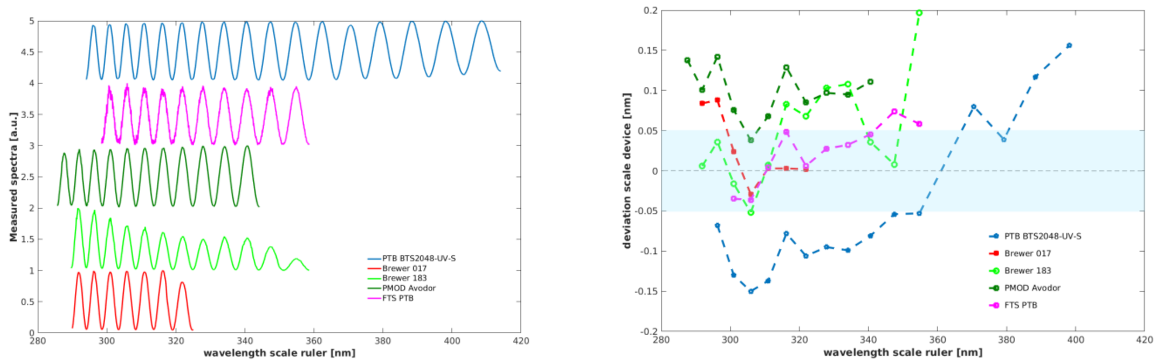


Figure 3.2.1.7: Results of the in-situ wavelength scale calibration of different instruments. The upper panel shows the spectra measured by the different types of instruments each covering its own spectral range. The lower panel shows the derived positions for the lines peaks. The light-blue interval, centred on 0 nm deviation, is just shown to guide the reader's eye and indicates the region within ± 0.05 nm deviation in the wavelength scale.

During TOC measurement campaign of Izaña, in September 2016, it has been proven how a properly designed wavelength ruler can be successfully used to calibrate the wavelength scale of different instruments. Considered the very diverse measurement conditions and the large diversity of the instruments characterized, the system has shown a very good portability and robustness for on-field measurements and surely show promise to further precise and accurate wavelength scale calibration in the UV range.

UV-LED Light Source

UV-LED source (ULS) has been designed to track the radiometric (spectral irradiance and wavelength drift) stability of array spectroradiometers in applications of measuring direct solar UV irradiance. The UV-LED device includes LED chips of different peak wavelengths put into a single package. The LEDs are mounted into temperature stabilized copper housing to maintain the stable performance of the chips (see Figure 3.2.1.9). The device is operated via external current source and temperature controller. Each LED chip is driven by its own micro-chip based current driver. Performance of the individual UV-LED chips as well as the whole unit under laboratory conditions was proven to be very good, i.e. stable and reproducible irradiance values were achieved after burn-in times.

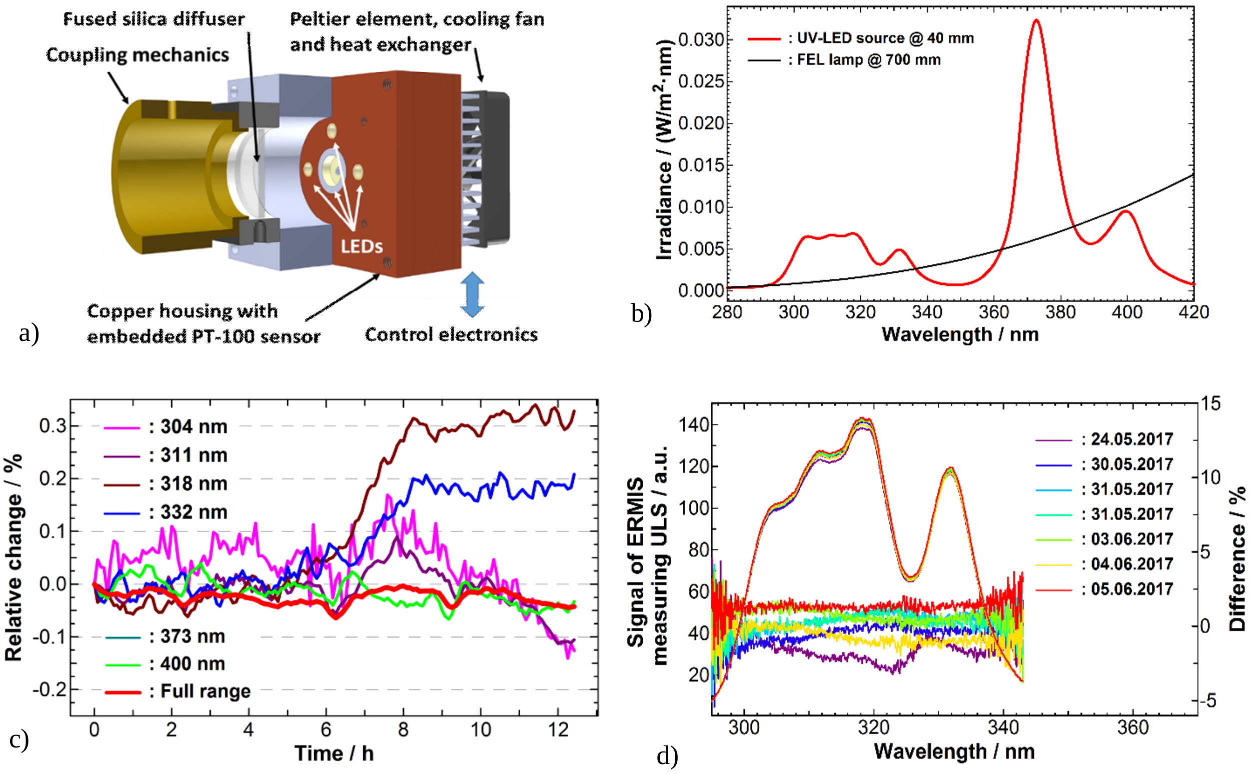


Figure 3.2.1.8 a) UV-LED source. Input optics of a spectroradiometer is reproducibly connected using coupling mechanics. **b)** ULS spectral irradiance compared to FEL lamp irradiance. c) Relative irradiance stability at LED peak wavelengths. Red curve shows irradiance changes integrated over 295 nm – 420 nm. d) ULS spectra (left axis) and its relative stability (right axis) measured with ERMIS array spectroradiometer during several days in Huelva measurement campaign. Measurement at 24.05.17 is done in laboratory in Davos where-as rest of measurements are carried out on field.

In the lab environment, the ULS showed excellent stability: ULS can keep its spectral irradiance stable within 0.3% over 10h of continuous run and its integrated irradiance measurements are repeatable within 0.1% over 5 consequent days. Its wavelength stability is better than 5 pm under stable conditions.

For field tests the ULS has been tested by PMOD/WRC with their newly developed ERMIS spectroradiometer (see section 3.2.2) at Izaña and at Huelva campaigns within the project. Huelva results show that at the ozone retrieval region the spectral difference (standard deviation) between measurements during the Huelva campaign is ±1% caused by the joint effect of ERMIS and ULS (see Figure 3.2.1.8).

A compact reference source based on UV-LEDs has been constructed to track radiometric stability of array spectroradiometers in applications of measuring direct solar UV irradiance in order to ensure reliable total column retrieval with well calibrated instruments. Potential commercialisation: an improved ULS with full spectral range could be valuable tool for wide range of array spectroradiometers by replacing the usage of standard lamps. Potential manufacturer should consider the costs of the ULS as currently the UV-LEDs on the market are still rather expensive.

3.2.2 Measurement Instrument

Why a new instrument: The new instrument (ERMIS) was designed with the objective of measuring direct solar irradiance in the spectral range 300 nm - 700 nm with a resolution of less than 0.3 nm, defined as the full width at half maximum (FWHM) and more than 5 pixels within the FWHM. In addition, the noise levels of the instrument to be less than the commercially available spectroradiometers. These specifications, are expected to reduce the uncertainty in DOAS retrievals of total column ozone in the wavelength range 300 nm to 340 nm, and of other trace gases such as nitrogen dioxide (NO2), oxygen dimer (O4) and water vapour (H2O) in the visible wavelength range between 400 nm to 670 nm.

Design of the instrument: The monochromator has been modelled using the ZEMAX® ray tracing software. The requirements with respect to the resolution are met with a selection of a Czerny-Turner design with a rotating grating (see Figure 3.2.2.1). To reduce the aberrations in the system, a parabolic mirror is used as collimating mirror, while a custom-made spherical mirror is used as focusing mirror. The high resolution and large oversampling on the detector is obtained by using a diffraction grating with 1800 lines/mm, dispersing a wavelength range of about 65 to 95 nm across the detector (Hamamatsu-S101411108) depending on the grating position. For minimizing the noise level of the spectroradiometer, the detector is cooled down to -20°C by using a 3-stage cooling system. The spectroradiometer is filled with nitrogen and pressurized to 1.5 bars to avoid condensation on the detector and deterioration of the optical components. The fore-optics of ERMIS consist of a telescope with a field of view of 1°, which images the radiation on an optical fibre. Two filter wheels are included in the optical path after the entrance optics; the first one contains neutral density filters to attenuate the radiation by up to a factor 10^3, while the second filter wheel contains several bandpass filters to select the optimal wavelength range depending on the selected measurement type.

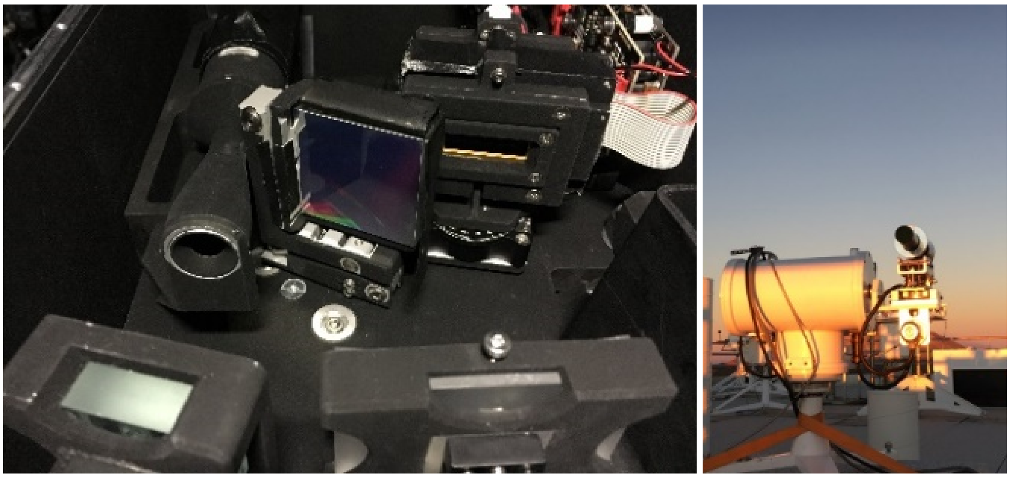


Figure 3.2.2.1: ERMIS monochromator (left) and ERMIS optical telescope on the solar tracker during Izaña campaign (right).

Performance of the instrument in the laboratory: ERMIS has been characterised in the laboratory with emphasis on the UV region for the ozone retrievals. The following tests have been performed:

- Detectors operational temperature with respect to noise level
- Wavelength characterisation
- Stray light contribution
- Direct irradiance calibration
- Field of view determination and optimisation

The performance of the detector with respect to the noise levels has been investigated for the temperature range of -20°C to +20°C by acquiring 100 dark signal measurements for different integration times. The operational temperature of less than -15°C has been selected as the noise level (mean standard deviation) reduction is exponentially decreasing with temperature reaching the level of 18-40 counts depending on the integration time at this temperature.
The wavelength characterisation and stray light contribution determination has been performed with the ATLAS tunable laser system of PMOD/WRC. The wavelength range in the default grating position is 294 nm to 390 nm with a FWHM of 0.23 nm ± 0.01 nm (2σ) which remains constant over the wavelength range 295-660 nm (Figure 3.2.2.2). The achieved over-sampling is 6-12 pixels within the FWHM of the slit function.
The line spread functions (LSF) of ERMIS for the wavelength range 295-390 nm have been measured. The presence of reflections of the dispersed light of the order 10^{-3} is evident (see Figure 3.2.2.3), which will be accounted for by applying the measured stray light correction which improves the ozone retrievals.

ERMIS was also calibrated to provide absolute direct irradiance and asses the stability of the instrument during transportation. During the Izaña 2016 and RBCC-E 2017 campaigns, its stability has been monitored daily through the ULS system (PTB, see section 3.2.1). ERMIS was stable within ±3% and reduction in its sensitivity of 5% due to transportation could be detected with the transportable monitoring system ULS.

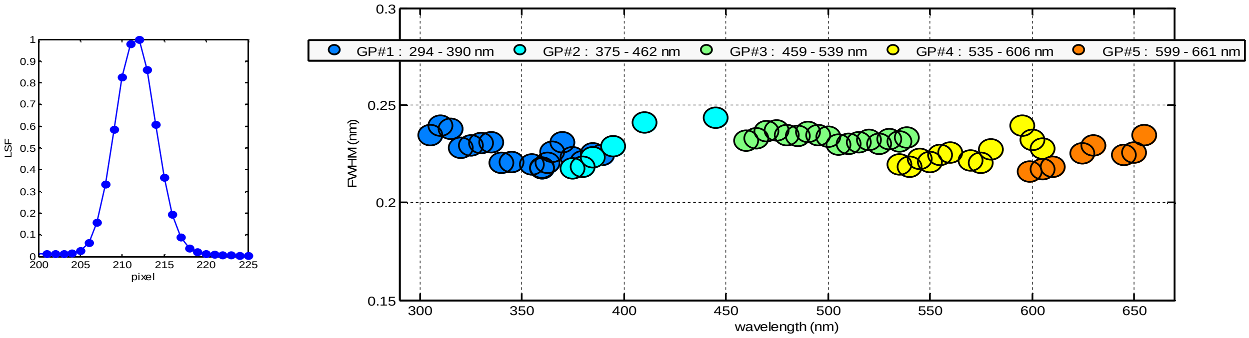


Figure 3.2.2.2.: ERMIS resolution (FWHM (nm)) for five selected grating position covering the spectral range 295-660nm (right). Example of slit function in the 295-390 nm range in pixel space demonstrating the achieved sampling (left).

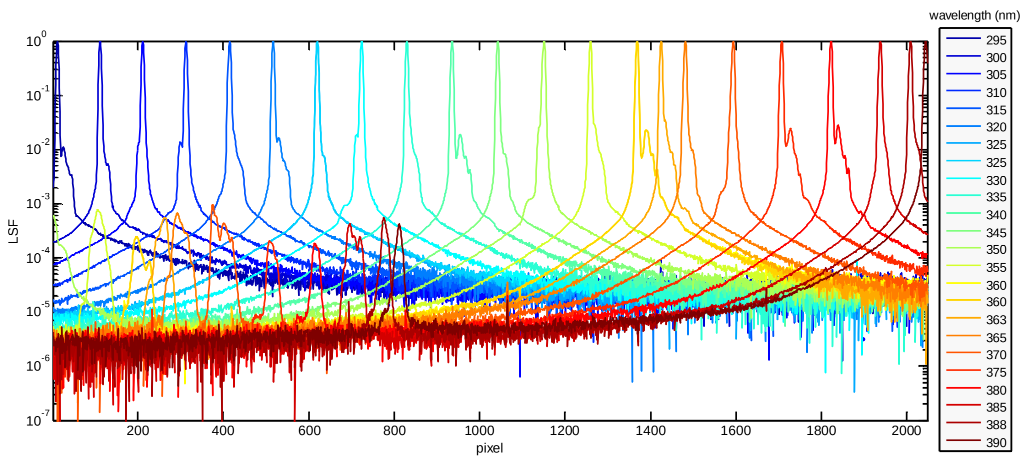


Figure 3.2.2.3: Line spread function of ERMIS for the primary wavelength range 295-390 nm

Results during the Izaña and RBCC-E campaigns: The ozone retrieval for ERMIS has been done using the DOAS technique and the QDOAS algorithm. The spectral fitting window used is 315-330 nm and the Bremen ozone cross sections at 228K and 223K was applied. The product of the analysis is the differential slant column density (DSCD) which is converted to vertical column by determining the amount of ozone in the reference spectrum using the Langley extrapolation technique over the DSCDs. The comparison of ERMIS with the reference Brewer triad in hourly mean values showed an agreement off 0.70 ± 0.93 DU over the whole period of ATMOZ- Izaña campaign. The RBCC-E campaign official results are not yet available however the performance of ERMIS can be assessed through comparison of the ozone product of QASUME which has a very stable performance, 1.10 ± 0.45 DU at Izaña. The two instruments are in good agreement, with the median difference to differ by 0.5 DU between the two campaigns and a similar spread (1σ) of 2.6 DU on average (Figure 3.2.2.3.).

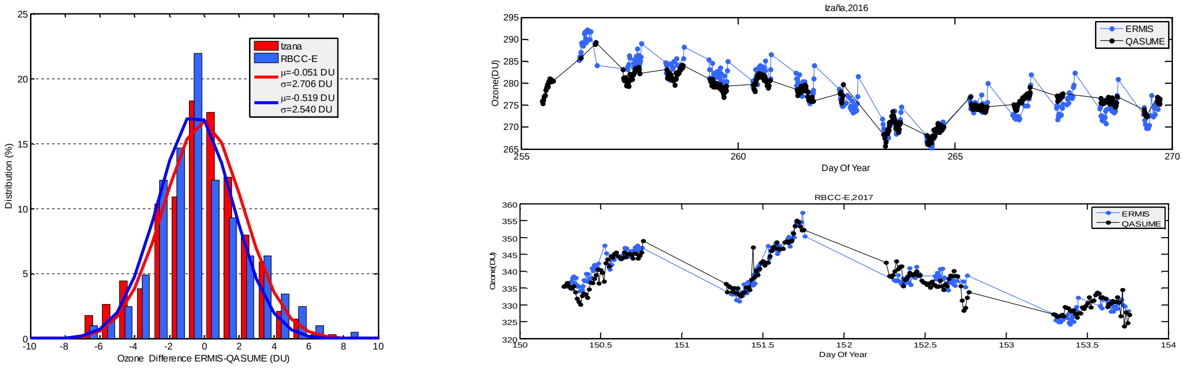


Figure 3.2.2.3: Distribution of the ozone difference between ERMIS and QASUME for the Izaña and RBCC-E campaigns (left). Time series of total column ozone measured by the two instruments during the campaigns.

The key feature of the new spectroradiometer:

- a resolution of 0.25 nm over the spectral range 295-660 nm
- low noise levels

gives an excellent platform for accurate retrievals of ozone as well as other trace gases absorbing in the operational region. The new instrument can serve as a new travel reference for instruments retrieving ozone from the full spectrum in the UV band (e.g. Pandora) as well as for instruments using the DOAS technique such as e.g. Phaethon.

The instrument has been manufactured successfully within the project with the support of the project partners and has participated in the two ATMOZ ozone field campaigns Izaña, 2016 and RBCC-E 2017 in Huelva 2017 providing very promising ozone retrievals. Due to the showed performance, the ozone community was informed about this next generation of highly accurate instrumentation. The device might serve as a future reference instruments not only for ozone but also for trace gases and aerosol optical depth in the framework of the world Radiation Center operated by PMOD/WRC.

<u>Other array spectroradiometer devices (Pandora and Phaethon)</u>

Ground-based TOC observations have been traditionally carried out by using two network instrument types: Dobson and Brewer spectrophotometers. Both instrument types use only a few selected wavelengths to retrieve the total column ozone in the atmosphere, making them very sensitive to wavelength misalignments and uncertainties in the ozone cross-sections. Carefully characterised and calibrated Instruments that measure the full solar spectrum between 300 nm and 350 nm, such as array spectroradiometers, can be used to retrieve the ozone content as well. Such measurements are expected to be less sensitive to these uncertainties since they provide a better constrained total ozone value from a larger parameter set. Thus, one of the tasks within the project was to characterise, correct and calibrate UV array spectroradiometers to enable the direct solar UV irradiance measurements with uncertainties required for the retrieval of the TOC. Array spectroradiometer characteristics of key importance for their application in the solar UV range include spectral stray light, bandwidth, wavelength assignment and linearity. PTB carried out such characterisations for two Pandora and one Phaethon instrument operated by REG{AUTH) that are employed for the TOC retrievals. Another Pandora system was also characterised by SFI Davos.

The linearity characterisations both at PTB and SFI Davos were carried out against a linear silicon detector using a laser. The setup allows to characterise the nonlinearity of array spectroradiometers both by varying the irradiance level (integration time kept at a constant value) and the integration time values (constant irradiance level). Such an approach is needed since both parameters can contribute to the nonlinearity of an array spectroradiometer and their individual contributions must be identified. The nonlinearity that can be corrected as a function of counts and can be as high as 5% in the usual range of counts (10^3 to 6.2 10^4), as shown in Figure 3.1.3.1.

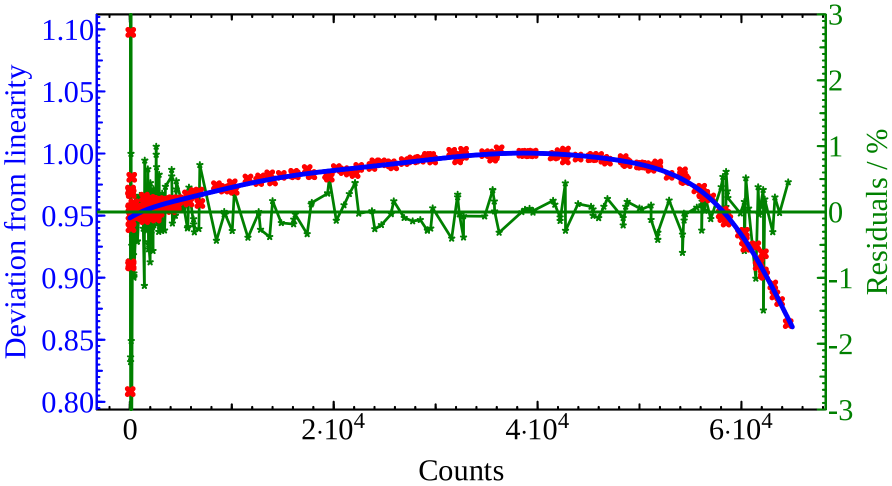


Figure 3.1.3.1. Determined nonlinearity (red crosses) of Phaethon spectroradiometer fitted by a 9th-order polynomial (blue line). The residuals of the fit are shown in green.

A poor suppression of the spectral stray light in the instrument can produce especially high errors in the UV spectral range. Hence, respective characterisation and correction techniques are required. The characterisations include measurements of the Line Spread Functions (LSFs) of the array spectroradiometers by wavelength tuneable lasers. This data is used to determine a stray light distribution matrix D (Figure 3.1.3.2) that allows to correct for the in-range spectral stray light. The out-of-range stray light is removed by bandpass filters. The LSFs data include also the bandpass information of the spectroradiometers.

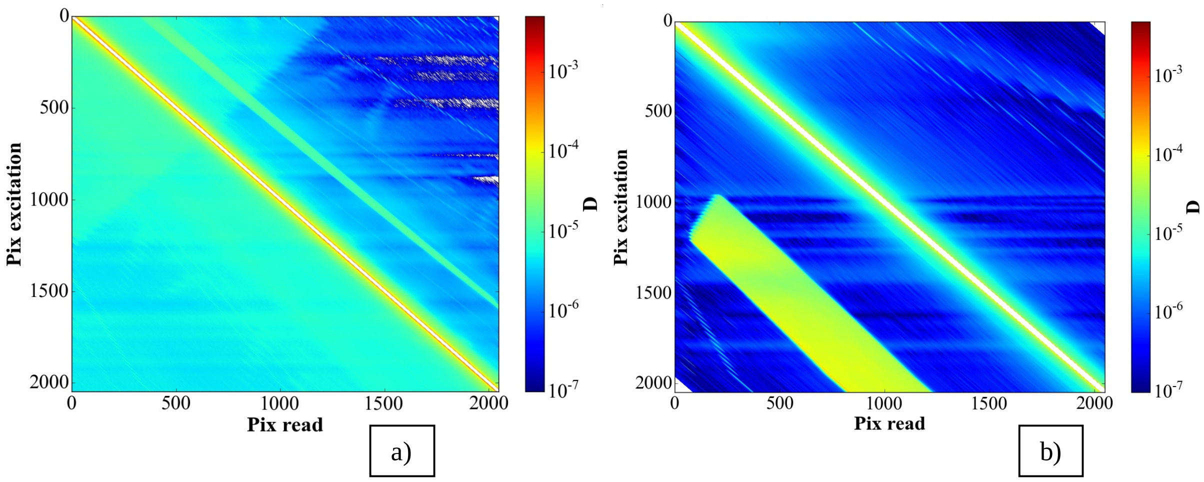


Figure 3.1.3.2. Stray light distribution matrices of Phaethon a) and Pandora b) spectroradiometers visualised as colour maps. The matrices show the relative amount of signal generated by every pixel of 2048 pixel detector arrays when light of a specific wavelength corresponding to one pixel (pixel excitation) is entering the instruments.

Pixel-to-wavelength assignement of array spectroradiometers with lowest uncertainties is of highest importance for the use of array array spectroradiometer data for the TOC retrievals. Such a wavelength calibration requires a dense grid of reference points on the wavelegnth scale as well as the respective bandpass functions. PTB and SFI Davos calibrated the array spectroradiometers using the wavelegth tuneable laser sources and laser wavemeters that allow determined the laser wavelength with an uncertainty of 0.01 nm. Based on a multitude of reference points a precise fit can be made (Figure 3.1.3.3).

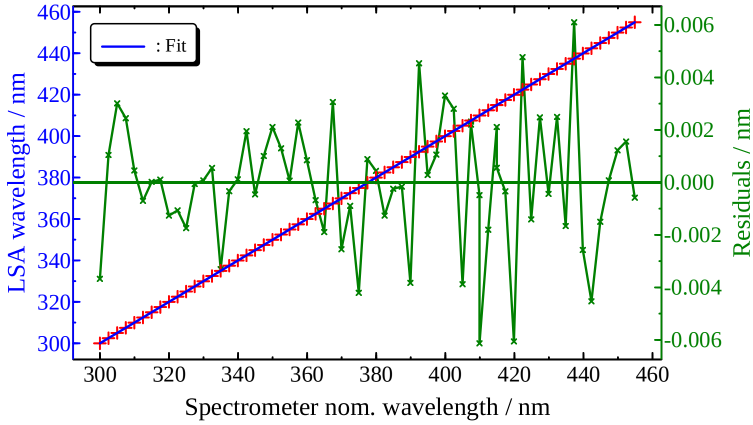


Figure 3.1.3.3. Wavelength scale calibration of Phaethon spectroradiometer. The measured points on the wavelength scale (red crosses) were fitted by a 6th-order polynomial (blue line). The residuals of the fit are shown in green.

For field calibrations of array spectroradiometer wavelength scales, VSL has developed a portable wavelength ruler that was also successfully used during the Izaña intercomparison campaign. The results of the field calibrations showed that the wavelength scale of even presumably stable instruments may still change and drift outside of the laboratories, thus, larger errors may be obtained without an in-field recalibration.

To achieve the results of this task, PTB, VSL, SFI Davos, Reg(ULL) and REG(AUTH) worked closely together. PTB has exchanged experience and details of the tuneable laser-based setups with SFI Davos so that dissemination of the services are available for a wide end-user community. PTB also supported REG(ULL) in establishing robust transfer standards for spectral irradiance calibration of the instruments leading to improved services. REG(AUTH) operated the PHAETON spectroradiometer and implemented the characterisations into their TOC retrieval algorithm.

Summary: The objective of developing field instruments for characterizing and validating network instruments globally at the corresponding measuring sites has been fully achieved. In particular, the portable radiation source for Dobson filed calibrations has been highly appreciated by the end-user community. Both, the portable radiation source and the wavelength calibration device were "Good News stories" for the EMRP community. Moreover, both devices may lead to a commercialization either in terms of a product or a calibration service by the corresponding National Metrology Institute. The newly developed high precision and low noise spectroradiometer might serve as a future reference instruments for ozone retrieval using the full spectrum in the UV band. Finally, the characterization of existing full spectrum ozone retrieval instruments led to an improvement of these devices.

3.3 New datasets for ozone retrieval

Why new datasets for ozone retrieval: In order to define common parameters to use, so that total ozone retrievals remain consistent among each instrument group, the datasets for the ozone determination needs to be re-measured with traceable quantities and uncertainties. Therefore the generation of new data sets of ozone absorption cross sections and an extra-terrestrial solar reference spectrum with state of the art measurement techniques were performed.

3.3.1 Improved ozone absorption cross sections

The spectroscopy is an important uncertainty contributor to the overall uncertainty budget of remotely sensed atmospheric trace gases. In current total ozone retrievals from ground and satellites there are three major ozone absorption cross-section datasets (derived from laboratory spectroscopic measurements) widely used, They are the Bass-Paur (BP) dataset the Brion-Daumant-Malicet (BDM) and the most recent SG data (Serdyuchenko and Gorshelev).

The BP dataset is regularly used in the standardized retrieval of Brewer and Dobson spectrophotometers, while the other datasets are used in satellite retrievals. Since the SG data provided the best consistency between Brewer and Dobson total ozone, the latter was recommended to be implemented in the standard retrieval by the International Ozone Commission (IOC). As part of the ATMOZ project the uncertainty budgets of the three major cross-section data were re-assessed by REG(UNIHB) and unified and published during the project in an international peer reviewed journal. In this study the uncertainty from the temperature parameterization (fitting a second degree polynomial to the cross-section data measured at selected temperatures) was included in the overall uncertainty budget. For the BDM and SG data the uncertainties were estimated at about 1.5%, while 2.1% was found for BP based upon detailed Monte Carlo simulations. At very low temperatures the uncertainty of the BDM data increases due to lack of data at the lowest temperatures (below 220 K).

Even though the SG data provides the best consistency between Brewer and Dobson results, there are some shortcomings to this dataset. At the low wavelength end of the Huggins band (below about 310 nm) the SG data have a rather low signal-to-noise ratio, which makes the data less attractive for satellite ozone profile retrievals that use wavelengths below 300 nm (not relevant for ground total ozone measurements). Another important goal performed by REG(UNIHB) was to possibly further reduce the uncertainties in the Huggins band (300-350 nm) with respect to the original SG data.

Measurements of new x-sections: One important improvement in the original experimental setups was the implementation of the ultra-stable Laser-Driven Light Source (LDLS). For wavelengths below about 300 nm, the echelle spectrometer were used while for the longer wavelengths up to 350 nm a Fourier Transform Spectrometer (FTS) was used. Due to some serious wavelength aliasing problems and CCD/intensifier degradation the results from the Echelle spectrometer turned out to be not usable, so that the wavelengths below 300 nm could not be measured with sufficient accuracy. REG(UNIHB), with the support of PTB, introduced several improvements to the FTS setup (covering 300-350 nm) and measurement procedure since the previous campaign. In particular, all measurements were performed with pure ozone samples, allowing for independent scaling of the relative (optical density) absorption spectra to cross-sections. Thermal insulation of the experimental cell and temperature management subsystem were upgraded to improve the temperature stability and homogeneity along the gas sample inside the cell (Fig. 3.3.1.1). In addition high-precision transducers were utilized to allow for reliable ozone pressure monitoring at target measurement ranges (1, 10, 100mbar).

REG(UNIHB) determined new ozone absorption cross-section spectra for eleven temperatures between 193K and 293K in steps of 10K covering the 295-300 nm wavelength range as shown in Figure 3.3.1.2.

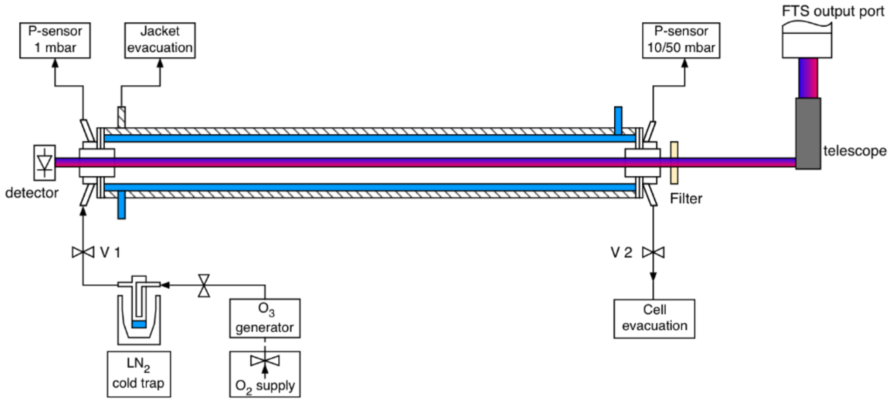


Fig. 3.3.1.1: Experimental set-up (single 135 cm long pass configuration). To cover the spectral range 300 to 350 nm measurements were done using single and dual pass configuration

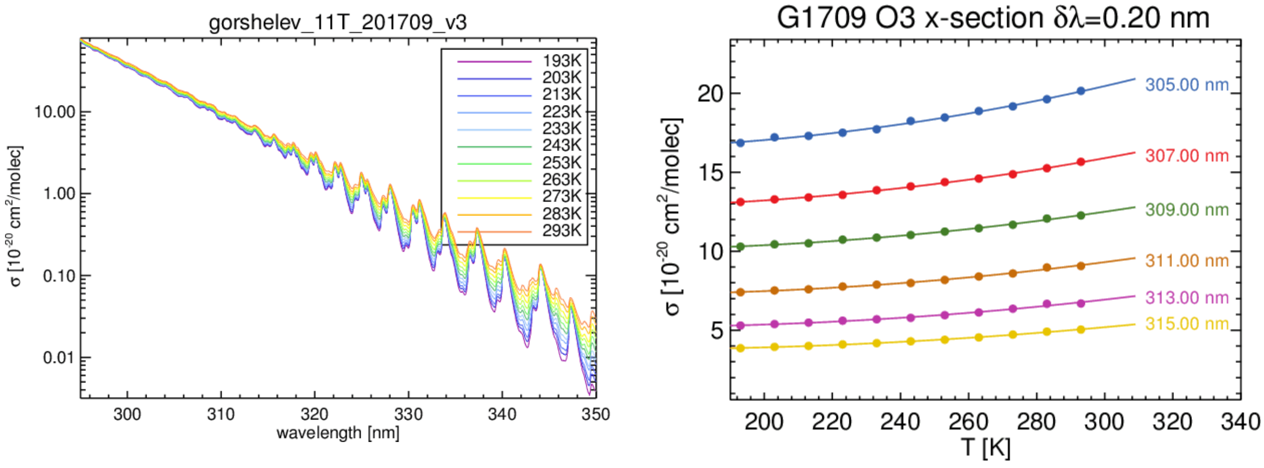


Fig. 3.3.1.2: New ozone absorption cross-section spectra at eleven temperatures from 193 K to 293 K (left). Temperature parameterisation (2^{nd} degree polynomial) at selected wavelengths (right).

Impact on ozone retrieval from the ground and satellite: The impact on ground and satellite retrievals were evaluated by comparing the new cross-section data as well as the BDM and SG data directly with the BP data as reference. The comparisons were done using a differential absorption technique similar to that used in satellite retrievals. The scaling factors then correspond to the expected ozone change in the retrieval due to the change in cross-section from BP. Table 3.3.1.1 summarises the results for the reference temperature 227 K. The comparisons were done for two spectral windows: 310-320 nm (contains the four Brewer wavelengths) and 325-334 nm (the DOAS spectral window for satellite total column retrievals). With respect to SG data, ozone retrieved with the new data will be higher by about 2-3% in both spectral windows. Using the new cross-section data, total ozone will be higher by about 2.3% than retrievals with BP at Brewer wavelengths. This is in agreement with campaign results using Brewer data. In the satellite DOAS retrieval window the ozone change is only a few tenths of a percent with respect to the usage of BP data.

Table 3.3.1.1: Expected ozone changes in the retrieval due to change in cross sections

Data	Ozone [%]	Shift [nm]	Fit RMS [a.u.]	Ozone [%]	Shift [nm]	Fit RMS [a.u.]
	310-320 nm			325-334 nm		
BDM	+1.4(12)	0.008(2)	0.0093	-0.2(6)	0.022(1)	0.030
SG	-0.7(12)	0.000(2)	0.0096	-1.6(6)	0.021(1)	0.027
ATMOZ	+2.3(11)	0.004(2)	0.0094	+0.3(6)	0.023(1)	0.034

3.3.2 New extra-terrestrial reference spectrum

Ozone retrieval from full spectrum measurements require the knowledge of the solar spectrum at the top op atmosphere in order to calculate the absorption due to the total column ozone.

The solar extra-terrestrial spectrum is usually measured from space-based instruments to avoid atmospheric absorption and scattering effects, especially at wavelengths shorter than 300 nm where ozone and oxygen in the atmosphere absorb all incident radiation. While pre-launch calibration and characterisation procedures reach very low uncertainties, once in space the possibilities of verifying or recalibrating such an instrument become very challenging. In contrast, while surface-based measurements of the solar irradiance have the disadvantage of needing to account for changing atmospheric conditions, the considerable advantage over space-based instruments is the possibility of recalibrating ground-based instruments and thereby validating and confirming their traceability to SI on a regular basis.

This project created ground-based direct spectral solar irradiance measurements obtained with the transportable reference double monochromator spectroradiometer QASUME over the wavelength range 300 nm to 500 nm and a high-resolution Fourier Transform Spectrometer (FTS) – in particular further developed in this project. A high-resolution absolute extra-terrestrial solar spectrum is then derived by applying the Langley-plot technique to the measurements of each instrument before combining them to a single solar spectrum.
The measurements were performed at the Izaña Atmospheric Observatory (IZO) located on the island of Tenerife, Canary Island, Spain from 12 to 25 September 2016. IZO is a high mountain station at an elevation of 2373 m above sea level, above a strong subtropical temperature inversion layer, which acts as a natural barrier for local pollution and low-level clouds.

QASUME: The transportable reference spectroradiometer QASUME consists of a double monochromator DM150 from Bentham with a resolution of 0.86 nm. A portable lamp system allows the calibration of the system while being deployed in the field. A collimator tube with a field of view of 2.5° is mounted on an optical tracker to measure the direct solar spectral irradiance.
A comprehensive uncertainty budget was calculated and published. The resulting expanded uncertainty for direct solar spectral irradiance measurements are 1.83% in the spectral range 300 nm to 500 nm.

FTS: The transportable Fourier Transform Spectroradiometer (FTS) consists of a Bruker Vertex80 Fourier Transform Spectroradiometer with a customised fibre based entrance optics for direct spectral irradiance measurements, i.e. a collimator tube with a field of view of approximately ±3.5°. The internal detector is a UG11-filtered GaP-photodiode covering the spectral range from 300 nm to 390 nm. The wavenumber resolution of the FTS was set to 2 cm^{-1} resulting in a wavelength resolution of less than 0.025 nm for this wavelength range. The wavelength scale of the FTS is inherently traceable to SI using a stabilised internal HeNe laser. The wavelength uncertainty is estimated to be equal or less than 0.01 nm. The radiometric calibration of the FTS was performed by a comparison with a calibrated spectroradiometer under natural sunlight condition. The data acquisition for a spectral irradiance measurement was <30s. This high resolution, low wavelength uncertainty and fast measurement time can be considered to be beyond state of the art compared to monochromator based spectroradiometers as well as array spectroradiometers.
Since the FTS was observed to suffer from an instability of the absolute scale, a monitor-filter radiometer was additionally developed. The monitor filter radiometer is a temperature controlled UG11 filtered GaP-photodiode mounted within a collimator tube. The filter radiometer correction factor is a scaling factor derived from the ratio of the measured filter radiometer current and the product of the measured radiometric corrected FTS spectrum and the spectral responsivity of the filter radiometer determined previously at PTB. The instability of the FTS spectral irradiance over time is then corrected by multiplying the raw FTS signal with this correction factor. The expanded uncertainty for measurements of the relative direct solar spectral irradiance was determined to be 2% to 4% in the spectral range 310 nm to 380 nm respectively. Below 310 nm the uncertainty of the FTS rises rapidly due to the low signal to noise ratio of the instrument.
During the Izaña campaign the FTS system successfully delivered high resolution direct solar spectral irradiance measurements that allowed the retrieval determination of a high-resolution extra-terrestrial spectrum.

Measurements: Direct solar irradiance measurements were performed in the period 14 to 24 September 2016. The extra-terrestrial solar spectrum was retrieved from the measurements by applying the Langley-Plot method to individual half-days in which there were cloud-free conditions.
In total 7 half-days with stable atmospheric conditions are available from QASUME for deriving a solar ET spectrum. Figure 3.3.2.1 shows the ratio of all 7 solar ET spectra to their average. The variability of the retrieved solar ET spectra variability originates both from the uncertainty of the measurement and instability of atmospheric conditions which is considered uncorrelated in between successive days. The resulting relative expanded uncertainty U (k=2) of the average QASUME solar ET spectrum is less than 2% between 310 nm and 500 nm, and rising to 4% at 300 nm.

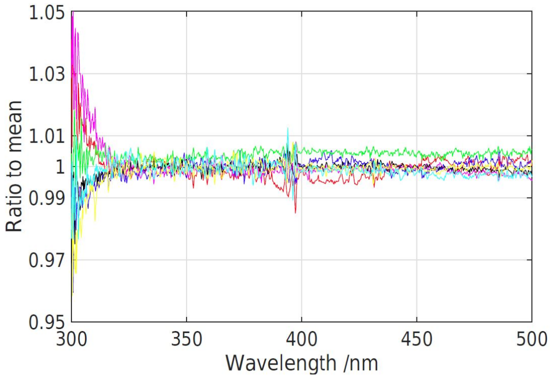


Figure 3.3.2.1: Ratio between solar spectra obtained from direct irradiance measurements with the QASUME spectroradiometer to their average during 7 half-days for the period 14 to 24 September 2016.

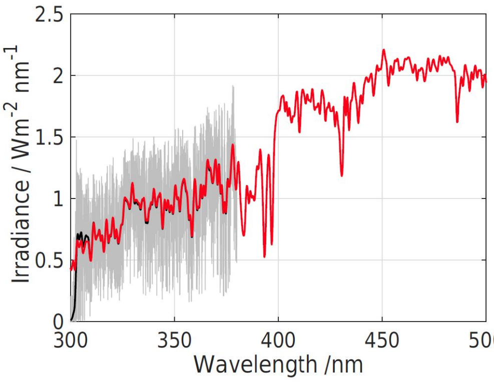


Figure 3.3.2.2: Solar spectra obtained from direct irradiance measurements with QASUME (red curve) and the FTS (grey curve). The black curve is calculated from convolving the high-resolution spectrum of the FTS with the QASUME slit function.

The same procedure was applied to the FTS measurements to derive a solar ET spectrum. In the case of the FTS, the measurements from 20 to 22 September with a spectral resolution of 0.025 nm were used. Figure 3.3.2.2 shows the QASUME derived solar ET spectrum, the high resolution FTS solar spectrum, and the FTS solar spectrum convolved with the slit function of the QASUME spectroradiometer.

The QASUMEFTS solar spectrum is a high resolution solar extra-terrestrial spectrum combined from ground-based measurements with a Fourier-transform spectrometer and a medium resolution scanning double monochromator spectroradiometer. As described here, the spectrum has the high spectral resolution from the measurements of the FTS and the absolute irradiance level from the QASUME measurements. The resulting QASUMEFTS spectrum has therefore an expanded uncertainty of 2% across the wavelength range from 310 nm to 500 nm, lower than any published solar extra-terrestrial spectra so far. This spectrum has been validated by comparison to solar spectra widely used in the community and can be used as a benchmark solar spectrum.

Summary: The objective of developing two new benchmark datasets for a traceable and consistent retrieval of total column ozone is fully achieved. First, a new ozone absorption cross section was measured in the laboratory and published to the ozone end-user community. The new ozone cross-section data are usable for all atmospheric ozone and trace gas retrievals (satellite and ground) that use spectral information from the 300 to 350 nm band. Second, a new extra-terrestrial solar reference spectrum has been generated from ground based UV measurements with new developed devices. The QASUMEFTS spectrum has been validated by comparison to solar spectra widely used in the community and can be considered as a benchmark solar spectrum, including a comprehensive uncertainty budget proofing the lowest uncertainty for a ground based extra-terrestrial spectrum so far.

3.4 Comprehensive Uncertainty Budget

Why comprehensive uncertainty budget: The knowledge of the overall uncertainty in estimation TOC is important to determine the significance of global ozone trends. During the last decades the decay of ozone is monitored to be around 5%. The recovery of the ozone layer is to be expected in the same order of magnitude. Therefore, the significance of proofing the healing of the ozone layer is first dependent on the uncertainty of monitoring TOC and second on the observation time.

Principally, the overall uncertainty is composed by

a) measurement uncertainties from the radiometry side of the UV measurements and
b) by the uncertainties originating from the atmospheric model and the corresponding retrieval.

Following, the uncertainties for the double ration technique (Dobsons and Brewers) and the full spectrum retrieval (e.g. array spectroradiometer and double monochromator) is calculated with different methods taking into account the uncertainties from the measurement and the model.

Brewer and Dobsons

Dobson and Brewer instruments perform TOC measurements at specific set of wavelengths pairs, where the absorption of UV light by O_3 is very different. If the measurements at two distinct couples of wavelengths are combined together, one gets the TOC (Ω,) by simply inverting Beer-Lambert's law. However, as far as the uncertainty estimate of the method is of concern, this approach neglects potential cross-correlations among nuance parameters and the desired measurand. Correlations are important because have a direct impact on the final measurement uncertainty. For instance, an anti-correlation can lead to an uncertainty reduction. In order to account for this effect, the process of determining TOC is re-defined as a method where one tries to match the measured quantity $y^{(m)} = N_1 - N_2$, where N_1 and N_2 are related to the actual counts measured by the instruments, and the model

$$y = (\Delta\alpha_1 - \Delta\alpha_2)\mu\Omega + (\Delta\beta_1 - \Delta\beta_2)mP / P_0 + \Delta\delta \sec(Z)$$

While the minimization of the distance, according to some metric, between $y^{(m)}$ and y leads to the value of the TOC, its sensitivity with respect to small variations of all parameters present in the model is directly linked to the uncertainty of the model used. There are some mathematical subtleties behind this approach, like ill-posedness and regularisation, but eventually a proper estimate of the said cross-correlations can be performed. As an example, Table 3.4.1 reports on the measured data generated by a Brewer instrument is shown. After applying the method described above, the cross-correlation affecting the TOC uncertainty can be derived for each single measurement.

The overall uncertainty of the Brewers is calculated by considering all the input uncertainties from the measurement and the retrieval model taking into account the correlation matrix as described above by carrying out a quadrature sum of different error sources. The first of them is the uncertainty of the Bass and Paur cross section. This cross section can be fitted by a quadratic function of the temperature which, at first approximation, we can select a value of -45 ºC. The uncertainty of the cross section can be obtained through a bi-quadratic function of the temperature (1.38 %). The uncertainty derived of the numerical integration method was obtained through Monte Carlo methods (Bootstraping Method) varying the central wavelength and the FWHM of each slit function as a function of its standard deviation (0.3 %). Finally, the uncertainty due to the variation of the ozone absorption coefficient with the wavelength was included. In this case the uncertainty is about 0.03%. Because, according to the climatology of the observatory, the effective temperature of the ozone layer is not always -45 ºC, and has to be include as an error source in the budget of the ozone absorption uncertainty. This uncertainty could vary between 0.09 % and 0.4 % depending of the climatological temperature of the ozone layer. With these error sources, the uncertainty of the ozone absorption coefficient is 1.43 % (Br#157), 1.39 % (Br#183) and 1.41 % (Br#185).

Table 3.4.1: Table of cross-correlation coefficients of a Brewer instrument

A1	Ozone	Rayleigh	Pressure	AOD	SZA	airmass	date	ETC	MS9
0.3385	370.0294557	1	1007.7		63.85116641	2.239717799	736108.3059	2950	5755.357874
0.3385	372.1812848	1	1007.7		60.95543503	2.038812779	736108.3165	2950	5518.564943
0.3385	373.0615912	1	1008.3		51.08351434	1.584120693	736108.3526	2950	4950.448975
0.3385	373.1912714	1	1008.3		49.1946256	1.523704952	736108.3596	2950	4874.824019
0.3385	374.0884515	1	1008.4		39.32730405	1.289980267	736108.3965	2950	4583.488348
0.3385	376.1539616	1	1008.5		38.72588121	1.279166188	736108.3988	2950	4578.738207
0.3385	376.000551	1	1008.8		35.49784253	1.226288118	736108.4114	2950	4510.772752
0.3385	374.8214293	1	1008.831		34.29958985	1.20869474	736108.4162	2950	4483.556275
0.3385	375.5418098	1	1008.874		33.19977888	1.193432359	736108.4207	2950	4467.101987
0.3385	375.1339048	1	1008.9		32.6389146	1.18596119	736108.423	2950	4455.967044
0.3385	376.9879481	1	1008.9		29.66998831	1.149690717	736108.4356	2950	4417.125158
0.3385	377.129491	1	1009		27.62181693	1.127638523	736108.4448	2950	4389.524537
0.3385	375.5391251	1	1009		23.31008837	1.088225195	736108.4674	2950	4333.351801
0.3385	376.6040015	1	1009.063		22.93873325	1.0852401	736108.4697	2950	4333.469013
0.3385	378.4930126	1	1008.8		20.19711531	1.065051071	736108.4934	2950	4314.542205

With all of this, we can obtain the overall uncertainty of the ozone measurements with Brewer spectrophotometer solving the equation

$$\sigma_{MS9}^2 = \sum_{i=1}^{N} \left(\frac{\partial MS9}{\partial x_i}\right)^2 \sigma_{x_i}^2 + 2\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial MS9}{\partial x_i} \frac{\partial MS9}{\partial x_j} \sigma_{x_i} \sigma_{x_j} R(x_i, x_j)$$

where, x_i are the different variables of the model including the Total Ozone Column (W) and $R(x_i,x_j)$ are the cross correlation coefficients between the variables. Given the uncertainties of all the variables, the overall uncertainty of the three Brewers is shown in the Figure 3.4.1.

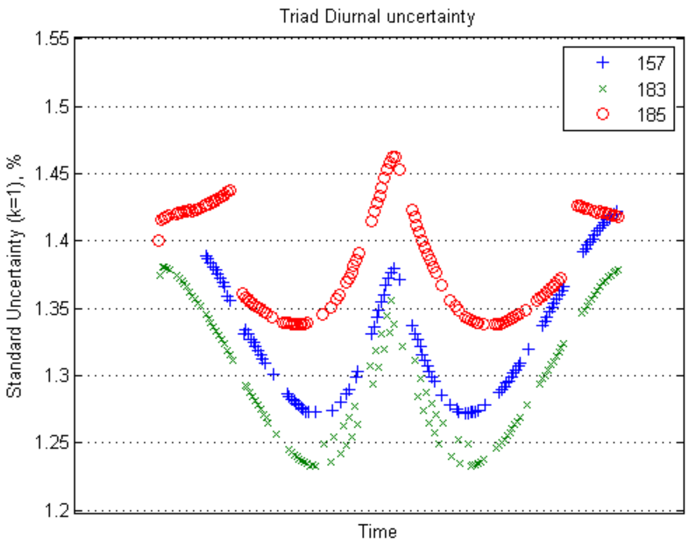


Figure 3.4.1.: The standard uncertainty of the Total Ozone Column including all the error sources for the Brewer #157 (blue), #183 (green) and #185 (red).

Full spectrum retrieval

In order to evaluate the overall uncertainty budget resulting from the full spectrum ozone retrieval, which is based on a linear least square fit ozone, two methods were chosen:

Traditional Monte-Carlo simulation: The measured spectra and the different model input parameters were varied within the random uncertainty of these parameters either originating from the radiometry uncertainty or from the model input uncertainties. Random variation means that a Gaussian distribution with the standard deviation (standard uncertainty, k=1) of the known uncertainty was generated and then randomly applied to each input spectrum. The random variation was repeated within 500 ensemble runs and the standard uncertainty (k=1) originating from the variation from the input parameters are given as the standard deviation over all runs.
The overall uncertainty of TOC retrieval of three different full spectrum instruments were measured at the first ATMOZ field campaign between 12 and 25 September 2016 at the Izaña Atmospheric Observatory, Canary Island Spain. Table 3.4.2 shows the uncertainty for different measurement and model input parameters as well as for the uncertainty of the retrieval fit. The overall standard uncertainty is 0.33 % for the high-end scanning spectroradiometer QASUME, 0.65% for a high-end array spectroradiometer, and 1.49% for a simple commercially available array spectroradiometer.

Monte Carlo simulation with correlated quantities: Within the ATMOZ project a new method taking into account effects of correlation between the measured spectral irradiance was investigated. The method is also based on a Monte Carlo simulation and firstly applied to estimate the uncertainties of coulometric quantities and further developed and applied to TOC retrieval within the ATMOZ project. The method assumes unknown correlations between the quantities and model their impact by using cumulative Fourier series with sinusoidal base functions. The weights of the Fourier series are selected in a N-dimensional coordinate system, where N displays the order of correlation between the quantities. Since the correlation are commonly unknown, the method separates the correlations in three parts: "Full"', “Unfavourable"' and "`Random"' and makes some assumption on the contribution of these three parts to the specific input uncertainty. The model applying correlated quantities is tested with spectral data measured with three different spectroradiometers at Izaña, Tenerife on Sept. 17, 2016 with the QASUME portable UV world reference spectroradiometer for the different input uncertainties. The combined standard uncertainty is around 1.8 % (=3.72 / 2 of the expanded uncertainty).

Table 3.4.2: Table of cross-correlation coefficients of a Brewer instrument

Source of Uncertainty	Standard Uncertainty u	QASUME	BTS	AVODOR
Measurement: QASUME	0.91 %	0.47 [DU]		
Measurement: BTS	1.24 %		0.68 [DU]	
Measurement: AVODOR	2.93 %			2.39 [DU]
Model: Extraterrestrial spectrum	1.00 %	0.12 [DU]	0.12 [DU]	0.12 [DU]
Model: Ozone absorption cross-section	1.50 %	0.25[DU]	0.25 [DU]	0.25 [DU]
Atmosphere: stratospheric temperature	1°C	0.70 [DU]	0.70 [DU]	0.70 [DU]
Atmosphere: Height of ozone layer	0.5 km	0.005 [DU]	0.005 [DU]	0.005 [DU]
Atmosphere: Rayleigh Scattering	0.5 %	0.04 [DU]	0.04 [DU]	0.04 [DU]
Atmosphere: Pressure	1.3 mbar	0.01 [DU]	0.01 [DU]	0.01 [DU]
Total All Input Parameter Uncert.		0.88 [DU]	1.01 [DU]	2.51 [DU]
Uncertainty of Fit	Computational	0.35 [DU]	1.54 [DU]	3.35 [DU]
Combined Standard Uncertainty (k=1)	Overall	0.94 [DU]	1.84 [DU]	4.18 [DU]
		0.33 %	**0.65 %**	**1.49 %**
Vaskuri et al. (no correlation) (k=1)	Overall	0.2%	0.35 %	1.05 %
Vaskuri et al. (correlation) (k=1)	Overall	0.66 %	1.24 %	2.94 %

The second method is a more general approach addressing the uncertainties of TOC than the first method, since the first method assumes no correlations between the radiometric quantities of the measurement or the model input parameters such as e.g. the cross sections. Therefore, the method taking into account correlations of the input uncertainties result in a higher uncertainty than when considering random noise as for the first method. When considering no correlations the uncertainties are similar as for the first method.

Summary: The objective of calculation the overall uncertainty for double ratio technique (Dobsons and Brewers) and full spectrum TOC retrieval (array spectroradiometer) is achieved for the Brewers and the several different instruments of full spectrum retrieval. For the Dobsons, the correlation matrix and a sensitivity analysis has been elaborated revealing an overall uncertainty of 1-2%, which is similar as the uncertainty for the Brewers. The combined uncertainty for full spectrum is around 0.7%, since the full spectrum exhibits more spectral information than only the four wavelengths from Dobsons and Brewers. Therefore the full spectrum instruments may serve as a new generation of instruments detecting the recovery of the ozone layer with more significance, than with Dobsons or Brewers.

3.5 Izaña intercomparison campaign

Direct solar spectra used to estimate the overall uncertainty of TOC retrieval of different instruments were measured at the first ATMOZ field campaign between 12 and 25 September 2016 at the Izaña Atmospheric Observatory, Canary Island Spain. The high mountain measurement site (2373 m.a.s.l) is above a subtropical inversion layer ensuring a stable atmosphere. Additionally, surrounding data, such as atmospheric soundings, pressure, aerosol optical depths etc. are collected nearby the station. The campaign was organized by Izaña Atmospheric Research Center of the Spanish Meteorological Agency (AEMET) and the World Radiation Center (PMOD-WRC) supported by the project

Sixteen instruments participated on the ATMOZ total ozone column intercomparison:

- Four total ozone reference instruments from World Dobson Calibration Center (WDCC) and the Regional Dobson Calibration Center –Europe,
- three Brewers from the RBCC-E Regional Brewer Calibration Center-E (RBCC-E)
- new CCD based instruments Pandora, Phaethon and BTS, and a new high-resolution array spectroradiometer systems (ERMIS) developed in the frame of the ATMOZ project.
- QASUME, portable UV word reference scanning spectroradiometer

The objective of the campaign was to compare the total ozone measurements of the participating instruments, to obtain a ground based high-resolution UV range extra-terrestrial spectrum and to apply the new techniques and devices to characterise the end-users instruments in the field.

Two data sets of total column ozone are analysed:

1. the operational algorithm using the standard settings for ozone retrieval
2. an updated data-set, which are the best possible homogenised data-set, where all instruments use the same state-of-the art ozone cross section, apply the instrument characterisation performed during the project and additional information of the available profile information (effective temperature and height) from ozone probe and other ancillary data.

Figure 3.5.1 first describes the current total ozone operational algorithm for the different instruments, the effect of the upgrades applied to the second data-set and finally the comparison both data-sets with the triad of Brewer spectrometers from RBCC-E. The figure, highlighting that the data-set 2 shows a better consistency than data-set one.

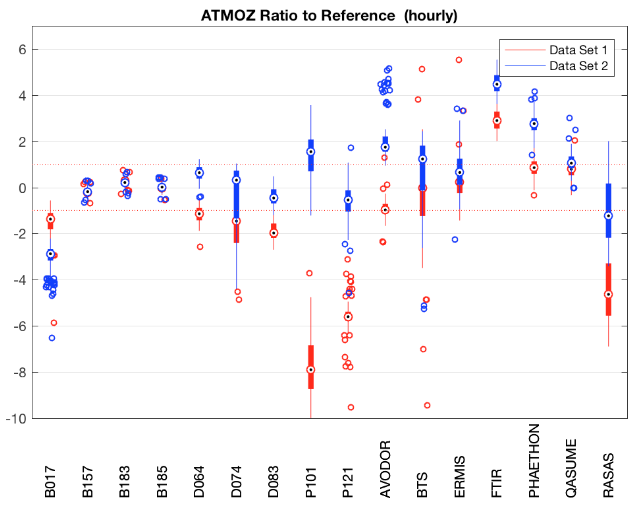


Figure 3.5.1.: Comparison of the performance of all instruments participating at the Izaña field campaign. Red denotes the performance of the instruments with standard settings, blue indicate the results with instrument settings or characterisations during the project

Summary: The intercomparison showed clearly that the overall objective of traceable total ozone column measurements and a homogenisation of the different ozone monitoring networks and its reference instruments has been achieved within the project.

3.6 Summary over all research

The overall objective of traceable total ozone column measurements and a homogenisation of the different ozone monitoring networks and its reference instruments has been achieved within the project.

- The measured bandwidth of the Dobson instruments led to a consistent retrieval of total column ozone within the Dobson network. The newly developed tuneable radiation source allows to characterise Dobson network instruments at regional Dobson intercomparisons at lower costs and less time than the characterisations in the laboratory at National Metrology Institutes.

- The thorough characterisation of the Brewer reference instruments led to the metrology based conclusion that the used bandwidths are consistent, the operational temperature correction can be applied and that a stray light correction for single Brewers has to be performed. This metrology based knowledge confirmed the standard operation procedure of the Brewer networks operators and proofs consistently the homogeneity of the Brewer ozone monitoring network.

- Three new devices for characterising total column ozone monitoring instruments in terms of bandwidth, center wavelength, absolute irradiance stability, stray light and temperature dependency have been developed and successfully tested within the project. In particular, the portable radiation source for Dobson filed calibrations has been highly appreciated by the end-user community. Additionally, the wavelength ruler displays a new device for characterising and calibrating the wavelength of ozone retrieving instruments in the UV band. Moreover, the UV-LED monitoring system allows to monitor and track the absolute stability of ozone instrumentations in order to ensure a traceable ozone record. Finally, the newly developed high precision and low noise spectroradiometer might serve as a future reference instruments for ozone retrieval using the full spectrum in the UV absorption band. All new devices opened new measurement capabilities at National Metrology Institutes, which can offer characterisation services for the ozone end-user community.

- The project has generated two new benchmark datasets, which are used for a traceable and consistent ozone retrieval. First, a new ozone absorption cross section was measured in the laboratory and published to the ozone end-user community. Second, a new extra-terrestrial solar reference spectrum has been generated from ground based UV measurements with new developed devices. The QASUMEFTS spectrum has been validated by comparison to solar spectra widely used in the community and can be considered as a benchmark solar spectrum, including a comprehensive uncertainty budget proofing the lowest uncertainty for a ground based extra-terrestrial spectrum so far.

- A comprehensive uncertainty budget for the two ozone monitoring networks (Dobsons and Brewers) and for the potential next generation of ozone retrievable instruments based on full spectrum measurements in the UV absorption band has been generated. The metrology based uncertainty budget allows now to establish the overall uncertainty of retrieving ozone with different measurement networks. In summary, total column ozone can be monitored with uncertainties around than 1%-2% with existing instruments and may be decreased to around 0.7% with new generations of instruments. The benchmark knowledge of the measurement uncertainty is of particular interest in determining the significance of global ozone trends in order to prove the recovery of the ozone layer due to the Montreal protocol.

3.7 Effective Cooperation

The project includes many examples of joint research, between project partners. As for the previous environmental EMRP project “Solar UV”, the coordinating organisation PMOD/WRC, serves as link between the Metrology and end-user communities, managing to extend the effective cooperation to collaborators and the end-user community. In particular in the field of ozone retrieval, were ozone is not only dependent on the raw UV measurements (metrology) but also on the retrieval model (atmospheric science), the cooperation between the Metrology Institutes and the atmospheric community was indispensable. Again PMOD/WRC has its focus in both fields of research and was able to establish a fruitful cooperation between the partners.

By the cooperation with several National Metrology Institutes the Dobson end-user instruments from collaborators of the project have been thoroughly characterized for bandwidth and center-wavelength tuneable laser sources, double monochromators and portable tuneable eradiation sources. The comparison of the different methods revealed that all methods are equivalent and the most time and cost efficient method (the portable tuneable radiation source) can be used for field characterization of this important quantity and will be offered a characterization method. The new characterization service was well received by the community and applied by several end-users. The benefit of the new characterizations was shown at the thorough ozone intercomparison on the Canary Island in Tenerife, assessing the improved characterization.

In the same context, a sound cooperation between several National Metrology Institutions and the Spanish Meteorological Agency AEMET (represented by REG(ULL)) and industry led to two a thorough characterization of the reference Brewer instruments in terms of wavelength and bandwidth, temperature dependency and filter behaviour, highlighting that the used standard operational procedure is adequate for the Brewer characterization. This proof could not have been achieved without the research undertaken within this project by the operators of the Brewer reference instruments solely.

The development of the different devices for wavelength calibration (wavelength ruler) and tracking the stability (UV-LED) was strongly encouraged by the needs of the end-users and were tested by end-users. The wavelength calibration devices developed by VSL were analysed with data from the Izaña campaign using data from 5 different instruments, which cannot be provided by the NMI themselves, resulting in a better understanding of the new devices. The results were presented in 2 Newsletters to the UV and ozone community. By the analysis and discussion between different partners, the relevance of tracking the wavelength and irradiance stability was considered as an important characterization in order to retrieve ozone and was communicated to the end-users, who are now be aware to address this problem in order to improve their ozone retrievals.

The new extra-terrestrial spectrum was only achievable by combining the QASUME reference instrument from SFI Davos with the newly developed Fourier Transform Spectrometer by PTB. This unique opportunity allowed to generate a benchmark extra-terrestrial spectrum with known and lowest uncertainty in the UV band relevant not only for ozone retrieval within 1% but also for modelling so solar UV spectra using radiative transfer models such as e.g. Libratran.

One collaborator from Industry (Gigahertz–Optics) collaborated with PTB for the preparation of the Izaña campaign were a new high-end array spectroradiometer was modified for direct solar UV spectrum measurements in order to test the ability of this commercially available instrument to retrieve ozone. Furthermore, the collaboration was extended to create a specific designed ozone retrieval algorithm for this new instrument by the help of PTB and support of PMOD/WRC.

The project partners deepened their collaboration within the National Metrology Institutes, Universities (REGs) and collaborators by several visits and measurement campaigns at the different institutes. For example, MeteoSwiss visited PTB for the characterization of the network Dobson D101. The results revealed a surprisingly large deviation from the assumed state of the instrument. REG(ULL) visited PTB, VSL and the manufacturer of the Brewers several times for the Brewer characterizations. Since REG(ULL) is operating the European Brewer reference triade, these personal visits strengthened the collaborations and knowledge exchange between these institutions. REG(AUTH), PTB and SFI DAVOS actively collaborated to fully characterise the PHAETON spectroradiometer.

In order to generate a comprehensive uncertainty budget of ozone retrieval from Dobsons, Brewers and full spectrum instruments, a deep collaboration was needed between two National Metrology Institutes (Aalto and VSL), the Dobson and Brewer end-users and PMOD/WRC was needed. The National Metrology Institutes contributed with their theoretical models and the end-users made a thorough evaluation of the expected input uncertainties. The difficulty of estimating the overall uncertainty budget from ozone was the measurements uncertainties had to be combined with the ozone retrieval model uncertainties. Due to the different knowledge of all involved partners, the problem could be addresses from a new perspective.

The main short-term impact focused on the end-users, which were trained during the project and at the intercomparison campaigns using the new characterization technologies the new datasets to improve and homogenize their ozone measurements in the field. The end-users are mainly operators of Dobson and Brewer reference and network instruments and researchers in the field of stratospheric ozone, who now have a close collaboration with National Metrology Institutes and have better access to their facilities and knowledge. The collaborations among partners and stakeholders were therefore very productive and scientific problems were discussed to ensure a goal-oriented achievement of the project's objectives. Most of the collaborations did not exist prior to the project and collaborations with some of the partners may be continued in further ozone projects.
Effective Cooperation

4 Actual and potential impact

Sixteen publications were published or submitted, and 25 contributions to conferences were made (13 oral and 12 poster presentations). The conferences included International Conference on Space Optics, Quadrennial Ozone Symposium, NEWRAD, and the International Conference on Meteorology, Climatology and Atmospheric Physics.

Presentations given at a number of ATMOZ forums and workshops can be downloaded from the project website (http://projects.pmodwrc.ch/atmoz/index.php/publications).

The WMO Regional Dobson Calibration Center for Europe, run by the Meteorological Observatory Hohenpeissenberg of Germany's National Meteorological Service DWD, invited the consortium to give a presentation about TuPS (Tunable Portable UV radiation Source) for characterisation of Dobsons
The work of the project was included in a published book Perspectives on Atmospheric Sciences, chapter title Total Ozone Retrieval from the Phaeton DOAS System.

12 articles were published in peer reviewed journals, including Atmospheric Measurement Techniques, Atmosphere-Ocean, Metrologia and Atmospheric Environment.

4.1 Metrology Achievements

Within this project metrological achievements for improving the traceability of total ozone column monitoring, in terms of thorough characterization of network reference instruments, developing new devices and methods, generating new benchmark datasets and calculation overall uncertainty budgets, have been made.

- Concerning the homogenization of ozone monitoring networks such as Brewers and Dobsons, the goal was to realize a metrology based traceability chain allowing the characterization and calibration of ozone monitoring instruments. The characterization of the Dobson instruments at the National Metrology laboratories with three different methods (tuneable laser, monochromator and portable tuneable radiation source) revealed that the bandwidth of all Dobsons deviate strongly from the nominal ones. Ozone retrieval with the measured bandwidth led to a homogenisation of the total column ozone measurements to the observations from the Brewer network. This achievement was highly appreciated by the Dobson end user community acknowledged with a letter of acknowledgement by the Regional Dobson intercomparison at Hohenpeissenberg by the Deutscher Wetterdienst (DWD), Germany, who was a collaborator of the project and member of the Scientific Advisory Group Ozone (SAG Ozone) dedicated by the World Meteorological Organisation (WMO). This new knowledge was presented and highlighted at the Quadrennial Ozone Symposium 2016 in Edinburgh and led to a peer reviewed publication in the special edition of the conference proceedings. The portable tuneable radiation source is a new device, which will be applied for in-situ Dobson characterisations during the official Dobson intercomparisons world-wide.

- The thorough characterization of the Brewer reference instruments led to the metrology based conclusion that the used bandwidths are consistent, the operational temperature correction can be applied and that a stray light correction for single Brewers needs to be done. This metrology based knowledge confirmed the standard operation procedure of the Brewer networks operators and proofs consistently the homogeneity of the Brewer ozone monitoring network.

- Existing full spectrum UV instruments (e.g. Pandora, Phaethon) have been radiometrically characterised highlighting that the non-linearity of these instruments is an important parameter in adequately retrieving ozone.

- The device for calibration of the wavelength scale and the new UV-LED device for tracking stability of ozone measuring instruments constitute new technologies to ensure the stability and traceability of total ozone, which is an improved metrology achievement for the ozone monitoring community including the full spectrum retrieval.

- Having characterized different reference instruments from the Dobson and Brewer network led to a homogenization of the two networks in better understanding the sources of uncertainty as shown in the Izaña field campaign.

- The generation of two benchmark datasets (ozone cross section and extra-terrestrial spectrum) with traceable estimation of the corresponding uncertainties, leads again to a homogenization of ozone retrieval with the new datasets.

In summary, worldwide ozone monitoring is now based on traceable instrument networks due to metrology characterization and calibrations with known uncertainties. The achievements of this project also allow the indication of the overall uncertainty in estimation total column ozone and to homogenize the networks within the states uncertainties. The development of a new high precision spectroradiometer (ERMIS), which will be a reference instrument not only for ozone but also for other trace gases will extend the activities of SFI Davos as the World Calibration Center for UV (WCC-UV) on behalf of the WMO in providing additional ozone observations at the standard UV calibration campaign at RBCCE. In the same context, the QASUME reference spectroradiometer – extended here for ozone observations - provides an additional portable instrument to monitor ozone with low uncertainties from full spectrum retrieval.

4.2 Early Impacts

Intercomparison

An ozone intercomparison was held at the Izaña Atmospheric Observatory located on the island of Tenerife, Canary Island, Spain from 12 to 25 September 2016. The intercomparison was attended by a large number of participants from the project and the end-user community, as well as from external industry. 15 instruments were operated on the measurement platform on the tower of the observatory: 4 Brewers (including the reference triade), 3 Dobsons, 7 full spectrum ozone retrieval instruments (e.g. Pandora, Phaethon) and the newly developed the Fourier Transform spectroradiometer. The participating instruments covered the traditional instrumentations as well as the next generation of instruments monitoring ozone. This campaign may be considered as the first thorough international intercomparison with this large number of different instruments.

The participants of the intercomparison were trained to work with the new developed devices, methods and test the results of the new characterisations performed prior to the campaign. Specifically following methods could be demonstrated and trained:

- Standard Irradiance calibration system
- New UV LED based monitoring and calibration system
- The new wavelength calibration devices
- The new high precision array spectroradiometer ERMIS
- The new Fourier Transform spectroradiometer to generate a high-resolution extra-terrestrial spectrum

The training with the tools and devices developed during the project were very well received and the feedback from the user community was very encouraging, demonstrating the value of this activity to everyone attending the intercomparison and workshop. Moreover, at the second intercomparison campaign at the regional Brewer intercomparison RBCC-E 2017 – the project results were additionally accepted by the Brewer community.

New devices and datasets

Two new devices for field characterisation were tested and promoted:

- Wavelength ruler for wavelength calibration
- Tuneable radiation source for slit function characterisation and calibration.

The portable radiation source for Dobson field calibrations has been highly appreciated by the end-user community (letter of acknowledgement by the scientific head of the WMO Regional Dobson Calibration Center for Europe, personal communication with members of the WMO scientific advisory group ozone, e.g. Australia). Both, the portable radiation source and the wavelength calibration device were “Good News stories” for the EMRP community. Moreover, both devices may lead to a commercialisation either in terms of a product or a calibration service by the corresponding National Metrology Institute. Exceptionally – and not provided in the project plan - the portable tuneable radiation source was used for characterizations of 9 more network Dobson instruments at the Regional Dobson Intercomparisons at Hohenpeissenberg and Huelva in 2017 indicating again that this new device is highly needed to improve the consistency and homogeneity of Dobson ozone readings in Europe and worldwide.

The portable world UV reference from the World Calibration Center for UV radiation (WCC-UV) at PMOD/WRC, QASUME is further equipped with a direct entrance optics tested during the Izaña field campaign for traceable ozone. Since the QASUME device is operationally used at the RBCC-E UV and ozone campaigns, QASUME can be considered as an additional independent instrument for the comparison of ozone observations. Additionally, the new precision array spectroradiometer ERMIS, developed within this project and tested at Izaña serves as a new reference high-resolution spectroradiometer not only for ozone retrieval comparison but also for other trace gases.

The methods, devices and uncertainty estimations investigated within the project, will be applied and further developed in a recently accepted four years project funded by the MeteoSwiss and led by PMOD/WRC in order to assess the past and future evolution of Ozone with state-of-the-art technology and modelling.

In analogy to the new devices the two new datasets (cross-section and extra-terrestrial spectrum) indicated an early impact on the ozone community in terms of testing the new datasets for the individual ozone retrievals at the Izaña intercomparison campaign. In particular the new extra-terrestrial spectrum can be considered a benchmark spectrum with traceable and known uncertainties.

Finally, the progresses and the results of the project and the intercomparison campaigns were continuously monitored and advised by key members of the Scientific Advisory Group Ozone (SAG Ozone) dedicated by the World Meteorological Organization (WMO). The feedback from the SAG ozone was always positive highlighting that the outcome of the project has a direct impact on the current decisions of the Advisory Group in terms of implementing the new methods (in particular the characterization of the Dobson wavelength and bandwidth). In turns, the advices of SAG ozone also guided the project towards more specific research for end-users needs.

Standards

The project partners from the National Metrology Institutes strengthened the impact of the project by the representation at 18 standard meeting and committees. For example, the World Meteorological Organisation (WMO), which is one of the most important global agency was informed three times about the content and implications of the project.

Since the project addresses key problems of the implementation of the Montreal protocol in reducing ozone depleting substance, the project was mentioned at the 10th Research Manager Meeting of the Vienna Convention and Montreal Protocol.

A second important platform for disseminating the results of the project on a Metrology level was the EURAMET TCPR meeting, represented several times by one of the project partner chairing the TCPR.

In order to confirm the strong relation between ozone monitoring and UV measurements this project was presented as part of the activities of the UV working group of the international Radiation Commission (IRC) at the annual IRC business meetings

These standards are the basis for the worldwide ozone and meteorology community to ensure the quality of ground based ozone measurements. These standards will guide the end-users in environmental science in their selection of new technologies and methods elaborated form metrology institutes.

4.3 Potential Impact

The step-change improvement in the calibration and characterisation of Dobson and Brewer instruments and the network instruments has provided the global observation network with improved ozone measurements with known uncertainties.

The development of novel spectroradiometer systems employing new techniques paves the way for including these instruments in the global ozone monitoring network, with a view to eventually replacing the traditional Dobson instruments, of which around 80 are currently deployed worldwide.

The result of this project is a step forward towards the implementation of the Montreal protocol and provides significant social benefits to the whole population with respect to solar UV induced skin deceases such as melanoma skin cancers.

5 Website address and contact details

For the public visibility of the project a website has been established. The website kept the end-users informed about project achievements, collaborators opportunities, events and project meetings.

In a password-protected area information for the project partners has been shared and archived.

The website is available under with following web-site:

http://projects.pmodwrc.ch/atmoz/index.php

The main contact for the project is the project coordinator from SFI Davos: Physikalisch-Meteorologisches Observatorium Davos and World Radiation Center (PMOD/WRC), Dorfstrasse 22 7276 Davos-Dorf; www.pmodwrc.ch :

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