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Carbon monoxide measurements onboard the CARIBIC passenger aircraft using UV resonance fluorescence

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Abstract

Goal of the project CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container) is to carry out regular and detailed observations of atmospheric composition (particles and gases) at cruising altitudes of
5 passenger aircraft, i.e., at 9–12 km. Continuous, fast measurement of CO is indispensable for the chemical characterization of encountered air masses, for the detection of plumes of polluted air and for studying troposphere-stratosphere transport. CO is measured by a commercial resonance fluorescence UV instrument modified for the use onboard passenger aircraft. Modifications were necessary to optimize the instrument
10 reliability allowing unattended operation for several days. The instrument has a precision of 1–2 ppbv at an integration time of 1 s. The response time to reach 66.6 % signal strength is 2 s. We describe the modifications of the instrument, the experiences made during its operation since December 2004, the quality control of CO measurements onboard CARIBIC, and suggest a regular service routine that guarantees long-term
15 high-quality data.

1 Introduction

Of the present three projects using passenger aircraft to sample the upper troposphere and lower stratosphere UT/LS (IGAC, 2007, and references therein), the CARIBIC project aims at routine measurements of a broad suite of atmospheric trace gases
20 and aerosol properties (Brenninkmeijer et al., 2007). Carbon monoxide, after ozone likely the second most measured atmospheric trace gas, is essential to characterize the chemical composition, origin, and fate of the sampled air masses (WMO, 2010). Throughout the troposphere CO is a major reaction partner in the photochemical cycles that control the concentrations of O_3 and OH radicals and by this the oxidation
25 capacity of the atmosphere (e.g., Logan et al., 1981; Parrish et al., 1998). It is emitted directly mostly from inefficient burning of fuels and is produced as an intermediate

of photo-oxidation of volatile organic compounds (e.g., Duncan et al., 2007). It has a relatively long atmospheric lifetime ranging at mid-latitudes from about 2 weeks in summer to several months in winter (Warneck, 1988) and is thus an excellent tracer for long-range transport (e.g., Smyth et al., 1999; Jacob et al., 2003; Jiang et al., 2007). Furthermore, CO is frequently used as a valuable tracer for anthropogenic pollution, and emissions from biomass and biofuel burning (e.g., Mauzerall et al., 1998; Smyth et al., 1999; Szopa et al., 2007).

The CO mixing ratio in the UT/LS varies from less than 30 ppbv in the lowermost stratosphere to more than 500 ppbv in the plumes of biomass burning (e.g., Mauzerall et al., 1998; Zahn et al., 2002a), and such contrasts can be found within distances of a few km when cutting through tropopause folds (e.g., Zahn et al., 2000; Roiger al., 2011). Combined with a cruising speed of typically $870\,\mathrm{km\,h^{-1}}$ ($240\,\mathrm{m\,s^{-1}}$) and unattended operation during a sequence of several flights, the CARIBIC instrument has to be fast, precise, accurate, and reliable.

CO is commonly measured by commercial instruments based on non-dispersive infrared absorption spectroscopy (NDIR), gas chromatography coupled with an HgO or flame ionization detector (FID) (by reducing CO to CH_4), and by resonance fluorescence in the vacuum ultraviolet (VUVRF) (Zellweger et al., 2009 and references therein). These four techniques were inter-compared at the high-altitude Jungfraujoch observatory (Switzerland) and found to agree within 2 % for one-hourly averages. Increasingly used are commercial instruments based on wavelength-scanned cavity ring-down spectroscopy (WS CRDS, Provencal et al., 2005; WMO, 2010). The original tunable diode laser absorption spectroscopy (TDLAS) was pioneered by several groups for research aircraft applications (Sachse et al., 1987, Wienhold et al., 1998). Indeed, at least three of these techniques (NDIR, TDLAS, VUVRF) are still used onboard aircraft, with their specific advantages and disadvantages (Nedelec et al., 2003; Holloway et al., 2000).

During the first phase of CARIBIC from 1997 to 2002, CO was measured by a gas chromatograph with HgO detector with a temporal resolution of 112 s corresponding

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to a measurement every ~ 30 km at cruising altitude (Zahn et al., 2002a). But as was well known, also because of concurrent highly resolved ozone measurements (1 s), small scale CO features are abundant. To better resolve the corresponding variations of CO concentrations and to cover the large span of the encountered mixing ratios, a fast linear response vacuum UV resonance fluorescence instrument (Volz and Kley, 1985; Gerbig et al., 1996, 1999; Holloway et al., 2000) was developed for the second phase of CARIBIC starting in December 2004. In this paper we describe the modifications of a commercially available instrument and its performance over more than 7 yr of operation and finally assess the data quality.

2 The CARIBIC container

The CARIBIC container housing altogether 15 instruments is flown aboard one of Lufthansa's Airbus 340–600. This aircraft was mechanically and electrically modified and equipped with a permanent air inlet system in November 2004 (Brenninkmeijer et al., 2007). The CARIBIC measurement container is deployed monthly on four consecutive long-range flights, such as e.g., Frankfurt – Caracas – Frankfurt – Osaka – Frankfurt, totaling about 40 flight hours. Each instrument in the container is equipped with its own computer that controls the measurement process and collects data. The instruments communicate via an Ethernet bus system with a master computer for control purposes. The master computer collects via the ARINC-428 bus system aircraft data on position, temperature, pressure, wind and some other parameters and records internal status data on temperatures at different places in the container and pressures at different points within the air sampling and distribution system. The communication between the master computer and the instruments is recorded and used for post-flight synchronization of the measurements. To avoid contamination of the instruments by strongly polluted air near airports, pumping systems are powered only above a pressure altitude of 750 hPa (~ 2.5 km). Like all equipment in the CARIBIC container, the CO analyzer had to pass a thorough safety certification process for the use onboard

a civil aircraft including tests of radiated and conducted electromagnetic interference (DO-160), and documentation with calculations to proof conformity with mechanical and electrical requirements as well as with the regulations of the use of hazardous materials.

3   CO instrument and its modifications

The fast-response UV resonance fluorescence (RF) instrument is based on a resonance-fluorescence of the $A^1\Pi \to X^1\Sigma$ transition of CO in the vacuum UV range around 150 nm (Volz and Kley, 1985). The instrument (Model AL 5002, Aero-Laser, Garmisch-Partenkirchen, Germany) is an improved version of the instrument described in detail by Gerbig et al. (1999). It uses a discharge resonance lamp excited by radio frequency (rf) radiation. Its light (135–175 nm) is collimated by an off-axis parabolic mirror into an optical filter consisting of 2 dielectric mirrors in series which confine the excitation wavelength to about 143–155 nm. The light beam is then focused by another off-axis parabolic mirror into the fluorescence cell. The fluorescent light with a wavelength ranging from 150 to 220 nm is imaged by a combination of two Suprasil lenses onto the photocathode of a small side-on photomultiplier tube with Suprasil window (Hamamatsu R6354). Suprasil optics and photomultiplier window block all excitation light below 175 nm. The use of the off-axis parabolic mirrors in the Aero-Laser instrument instead of the CaF_2 lenses shown in Fig. 1 of Gerbig et al. (1999) further improved the transmission of the excitation optics. The replacement of the original Hamamatsu R759 photomultiplier by R6354 improved the maximum quantum efficiency from about 15 to 35 %.

Figure 1 shows schematically the lay-out of the sample air flow through the instrument. Sample air is taken from the trace gas probe diffuser tube using a perpendicular 3/8″ PFA lined pick up tube (heated to 40 °C) (Brenninkmeijer et al., 2007). The trace gas sampling line from the inlet, which is mounted underneath the aircraft in front of the measurement container, likewise is fitted with a PFA liner and all tubing is heated.

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Depending on the cruising altitude the air sample inlet pressure (sum of ambient and ram pressure) varies between ∼ 220 and 300 hPa. The pressure in the fluorescence cell is kept constant at 10 hPa by a back pressure controller (PC) at its entrance. Down-flow of the pressure controller the sample air is directed either via a needle valve or via a zero-air trap (stainless steel tube, ID 10 mm) filled with 9.1 g of Sofnocat (Molecular Products Ltd.) catalyst (Foulger and Simmonds, 1993) into the fluorescent cell. The needle valve (NV) is adjusted to match the flow resistance of the parallel zero-air trap. The air from the optical cell and the gas from the rf discharge is disposed by a di-aphragm pump (Vacuubrand, MD4) installed in the CARIBIC container.

The following modifications have been made to the device.

The original housing of the instrument was replaced by an electromagnetic interfer-ence (EMI) proofed 19″ housing (W 480 × D 600 × H 177 mm) with additional space for DC/DC converters, an EMI filter, a RS-232 to Ethernet converter that interfaces the instrument to the container data bus (custom made RS485 with Code Division Multiple Access), memory cards for housekeeping data and signals, and aircraft fuse/switch (ETA Model 482).

The original CaF_2 lamp window was replaced by a MgF_2 window because of its higher VUV transmission (Samson, 1967). The detector window of the cell was origi-nally sealed using an adhesive. This sealing frequently caused leaks, probably because of the large temperature variations of the instrument ranging from less than 15 °C to occasionally over 35 °C depending on ambient conditions. A Viton o-ring seal fitting installed in the existing groove solved this problem.

An additional three-way valve (top left corner of Fig. 1) in the internal inlet tubing of the instrument enables the measurement of calibration gas during the flight. The back pressure controller at the entrance of the fluorescence cell keeps the pressure in the cell constant even if the pressures of the sample air and the calibration gas are differ-ent. We found that the calibration gas becomes contaminated during the period of up to a few days between the final preflight conformation test of the container and the first flight, which lead to excessive drifts in zero and calibration signals during the first two

calibration cycles. The contamination was dependent on the type and manufacturer of the pressure regulator used on the cylinder filled with CO calibration gas. The contamination from a stainless steel membrane pressure regulator manufactured by AGA was the smallest of the tested regulators but still did not allow reliable measurements during the first two calibration cycles. Flushing the calibration gas tubing three times with the calibration gas a few hours before the first flight removed this problem.

We do not apply drying of the sample air, as usually done by using Nafion driers or Drierite (e.g., Holloway et al., 2000), because the air at altitudes between 9 and 12 km is dry. The typical mixing ratios at the altitudes are 10–100 ppmv, with very rare and short episodes reaching 1000 ppmv (Schuck et al., 2009). According to Gerbig et al. (1999) such low humidity does not influence the signal. We have replicated their laboratory test and, as them, found no change in zero air and calibration gas signals by saturating zero air and calibration gas with water at 20 °C (which corresponds to $\sim 20\,000$ ppmv H_2O).

Until February 2010 the optical path between the lamp and the fluorescence cell as well as between the cell and the photomultiplier had been flushed by nitrogen to eliminate the absorption of the lamp light by oxygen. To reduce the number of gas cylinders in the container, the already installed cylinder filled with a gas mixture of 2.5 % CO_2 in Ar initially only used to supply the discharge lamp was from then on also used for flushing the outside optical path. Both the lamp and the optics flushing flow rates are kept constant at 30 cm^3 min^{-1} STP using flow controllers.

The sample and calibration gas flow rates are set to ~ 100 cm^3 (STP) min^{-1}. To sustain the flows of sampling gas, flushing gas, and lamp gas up to an altitude of 12 km, a more powerful pump (Vacuubrand Model MD4) than supplied was installed. We also found it useful to increase the operating temperature of the Sofnocat catalyst from ambient to 80 °C.

The modified instrument now weighs 20.5 kg and consumes less than 450 W (28 VDC) during the warm-up and ~ 200 W during the continuous operation. To avoid problems with radiated and conducted electromagnetic interference, the entire assembly of

the rf generator, the lamp, the fluorescent cell, and the photomultiplier was made radio frequency tight. An additional EMI filter (Yumpen model YC06T1L2) at the power socket blocks the conducted interference. The instrument underwent extensive tests on conducted and emitted electromagnetic interference based on DO-160 regulation on 2 occasions as a part of the entire container instrumentation in a large certified EMI facility.

The original detector signal, i.e., the count frequency, and the status signals such as the pressure in the cell, the flow rates, and the temperatures of the photomultiplier and the lamp are recorded (count frequency with 1 Hz, status signals with 0.1 Hz) and processed in a post-flight data analysis. The instrument is calibrated in flight every 25 min using a working standard with a nominal mixing ratio of 250 ppbv CO in air (Scott Marrin). The calibration cycle consists of a calibration measurement for 80 s followed by zero measurement for another 80 s. Only the final 60 s averages of each calibration sequence are taken for calculating the zero signal and sensitivity. The CO mixing ratio during flight is calculated from the measured signal by subtracting the average zero signal and applying the average span of the calibrations bracketing the measurement interval of 25 min.

4 Long-term performance during CARIBIC flights

The instrument temperature, which in turn depends on the temperature of the cargo bay, is the major parameter influencing the zero and span signals. As an example Fig. 2 shows the instrument sensitivity and the zero signal measured during the different calibration sequences as well as the continuously measured temperatures of the photomultiplier and the lamp during flight #347 from Frankfurt to Bogotá on 16 June 2011. During the ~ 10 h flight the instrument sensitivity and zero signal varied by $\sim 5\%$ and 4%, respectively. The origin of these drifts could not unambiguously be delimited. There is a negative correlation of both parameters with the temperatures of the photomultiplier and the lamp in the order of $-1\% \, \text{K}^{-1}$. The high stability of the photomultiplier

specified by Hamamatsu is far too small to account for this drift. We rather believe that the temperature of the lamp and the following optics (alignment) causes a relevant change in the light intensity and/or light transmission to the measurement cell. Gerbig et al. (1996, 1999) also found a strong correlation of the sensitivity or light intensity, respectively, with the pressure in the lamp that in turn is influenced by the lamp temperature. The drifts shown in Fig. 2 are typical for most of the flights with controlled cargo bay temperature. The temperature of the cargo bay was not well controlled during several flights and in these cases the drifts of span and zero signals could be twice as large.

During this flight #347 the average span and zero signals amounted to 27 246 and 5011 counts s^{-1}, respectively, which results in a sensitivity of 105 counts ppbv^{-1} s^{-1}, which is a factor of $\sim$ 50 higher compared to the first instruments described by Volz and Kley (1986) and Gerbig et al. (1996). The zero signal noise of $\pm$70 counts s^{-1} thus causes a noise of $\sim$ 0.7 ppbv at 1s. The additional noise from the photon statistics certainly depends on the CO concentration and varies between 0.53 ppbv at 1 s and 30 ppbv ($30\,\text{ppbv}/\sqrt{30 \cdot 105}$) and 1.38 ppbv at 1 s and 200 ppbv ($200\,\text{ppbv}/\sqrt{200 \cdot 105}$). The ambient mixing ratios of 30 and 200 ppbv can thus be measured with a precision of $\sim$ 1.2 and $\sim$ 2.1 ppbv, respectively.

This high precision due to photon statistic is also reached during flight. During flight #116 from Santiago de Chile to São Paulo on June 2005 21, the CARIBIC aircraft sampled an extremely well mixed flight section close to the tropopause of the Southern Hemisphere from 18:47:41 to 19:11:52 UTC, i.e., over $\sim$ 24 min, and measured an almost constant CO mixing ratio of 47.9 $\pm$ 1.6 ppbv. Counting statistics suggested a precision of 0.65 ppbv ($47.9\,\text{ppbv}/\sqrt{47.9 \cdot 115}$) plus the zero signal noise of $\sim$ 0.7 ppbv (see above), which in sum is only slightly less than the measured noise of 1.6 ppbv. This measured standard deviation is the sum of instrument noise and atmospheric variability over the quite long sampling period of $\sim$ 24 min (or $\sim$ 350 km along the flight path). We can thus conclude that the precision of the CO measurements during the

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regular CARIBIC flights is determined by counting statistics which is controlled by the instantaneous sensitivity.

A further crucial feature is the long-term stability of the device, i.e., the change in the zero signal and sensitivity during the regular CARIBIC flights. Figure 3 shows the zero signal and sensitivity for all CARIBIC flights between May 2005 and December 2011. The zero signal and sensitivity decreased strongly from the initial values of $\sim 115\,\mathrm{counts\,s^{-1}\,ppbv^{-1}}$ and $4500\,\mathrm{counts\,s^{-1}}$, respectively, in May 2005 to less than $15\,\mathrm{counts\,s^{-1}\,ppbv^{-1}}$ and $1000\,\mathrm{counts\,s^{-1}}$ in May 2008, respectively. The precision of the CO measurements deteriorated correspondingly with the worsening photon statistics from initial 0.5 ppbv to 2 ppbv for 1 s integrating time. The dark photomultiplier signal remained constant at $76\,\mathrm{counts\,s^{-1}}$ (not shown) implying that the lamp or the transmission of the optical system deteriorated over the three years of use. Figure 3 shows that the relation between the zero and sensitivity deterioration and the number of operating hours is not linear suggesting that other factors might also play a role such as the purity of the argon/CO_2 gas mixture used to operate the lamp.

To restore the sensitivity, first the parabolic off-axis mirror collimating the light of the lamp was changed in February 2008 with hardly any effect. The original sensitivity was, however, nearly restored by renewing the MgF_2 window of the lamp in June 2008. Inspection of the old window under a microscope revealed a four dot grey-brown pattern coinciding with the four gas inlet holes. Grinding and polishing of the exposed side of the window did neither remove the pattern, nor restored the original sensitivity or light intensity, respectively. We thus surmise that the transparency of this window had been impaired by the formation of color centers as had been observed when using LiF windows (Samson, 1967; Warneck, 1965). The sensitivity decreased again after June 2008 until October 2009 although the zero signal did not change much during this period. Since May 2010 until February 2011 the sensitivity remained nearly constant whereas the zero signal decreased by some 20 %. The exchange of the MgF_2 window in February 2011 restored the original sensitivity again and led to somewhat higher zero signal, both of which remained nearly constant afterwards. We thus conclude that

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the actual property of the MgF_2 lamp window largely determines the sensitivity of the device and has to be exchanged after a certain period of operation. Based on our experience (Fig. 3), the transmission of the MgF_2 lamp window decreased by $\sim 3\%$ per flight sequence of four consecutive long-range flights, i.e., altogether 30–40 flight hours.

The response time of the instrument, here the time to reach 66.6 % of the final signal, was determined to be 2 s by stepwise increasing the concentration during a test in the laboratory. The stepwise reduction of the concentration yielded the same response time of 2 s. Figure 4 shows an actual case onboard the CARIBIC aircraft, namely O_3 and CO measurements during a section of flight #185 from Guangzhou to Frankfurt on 8 March 2007. The aircraft flew through a very thin laminae structure, most likely generated by a gravity wave, concomitant with rapid changes of O_3 which was tightly anti-correlated with CO. Ozone was measured by a fast chemiluminescence instrument with a temporal resolution of 0.2 s (Zahn et al., 2002b; Brenninkmeijer et al., 2007). The ozone peak at 01:34:48 UTC was accompanied by a sharp dip in the CO mixing ratios confirming that the response time in flight is indeed about 2 s.

Linearity of the instrument was tested off-line using a 15 ppmv CO in air calibration gas (Scott Marrin) diluted by zero air to get a range of 43.5 to 290.6 ppbv of CO. The deviation from the linearity varied between −0.9 at the lowest and +0.7 % at the highest concentrations and the average deviation over the tests concentration range was with $0.30 \pm 0.49\%$ insignificant.

5 Accuracy of the CARIBIC CO data

The accuracy of CO measurements has been an ongoing challenge (e.g., Novelli et al., 2003) in general. The main reasons were the drift in CO standards as mixtures are often not stable in high-pressure gas cylinders. The non-linearity of the HgO detectors used frequently in the past as the sole detector system contributed to further uncertainties. Table 1 presents the results of a main round robin experiment involving

a large number of laboratories, including EMPA (Switzerland, WMO audit institution) and NOAA-ESRL (US, the supplier of standard mixtures based on gravimetry). The results of our institute (MPI) are given with the combined uncertainty of measurement and calibration, the EMPA results with their analytical precision, and the NOAA results include an estimate of uncertainty in the CO scale (WMO, 2010). Most of MPI measurements agree within the given uncertainties with those by EMPA. This is not surprising given that the MPI calibration standard of 155.8 ± 0.5 ppb was tied to EMPA standard of 352.5 ppb (cylinder CA 06490). Differences between MPI and NOAA measurements are somewhat larger but, considering the individual uncertainties given by both laboratories, they still lie mostly within the WMO data quality objectives (DQO) of ± 2 ppbv for measurements in marine boundary layer and at other remote sites (WMO, 2010).

The round-robin experiment confirmed that the old MPI gas standard mixture from Scott Marin with a nominal mixing ratio of 250 ppbv had in fact a mixing ratio of 263.5 ppb, i.e., was by 5.4 % higher. Consequently, all CARIBIC phase 2 measurements (since May 2005) published until March 2010 must be corrected by a factor of 1.054. From then on all data provided are on the NOAA 2004 scale.

Since May 2005 altogether 250 CARIBIC flights have been conducted. The CO instrument has failed during 7 flights, which results in its availability of 97 %. During 3 individual flights the data loss can be attributed to instrument malfunction: during one flight the lamp did ignite and during two flights the flow controllers did not work. All other data loss was due to external factors such as switched off pump due to malfunction of the system controller.

A practical problem in the operation of the instrument remains the ignition of the discharge lamp. On average, it takes ∼ 11 min to ignite the lamp but on occasion it may take only 1 min or as much as 30 min. We tried and failed to get a faster and more predictable ignition by repeated readjusting the rf coupling to the discharge capillary. This can be done now only when the lamp encasement is open. We note that the encasement itself is a part of the rf resonator and the adjustment should be possible

from outside without opening it, e.g., by screws, as is the usual practice with microwave resonators (Samson, 1967).

6 Conclusions

The commercial vacuum UV resonance fluorescence instrument with modifications de-
scribed here has proved to be able to provide fast (2 s response time) and accurate
(within ±2 ppbv data quality objectives stipulated by WMO, 2010) measurements of
CO mixing ratios onboard the CARIBIC passenger aircraft. The experience accumu-
lated over more than 6 yr of operation shows that the instrument was reliable with 97 %
data availability. Decreasing sensitivity and zero signals were attributed to the deteri-
orating transparency of the MgF_2 entrance window of the fluorescent cell and could
be restored by replacing this window. Owing to the loss of transparency of ~ 3 % per
flight sequence of four consecutive long range flights observed during CARIBIC, it is
advised to do this regularly. During CARIBIC with ~ 5 operational days per month (in-
cluding ground tests), this window exchange has to be done each 1.5 yr. The lifetime
of the window may depend on the purity of the gas with which the lamp is operated
and on the operating conditions. On this point we have no solid information from other
users of this type of instrument. Although the problem of unpredictable and sometimes
long delay before ignition of the rf discharge in the lamp has not been resolved so far,
the overall performance and use of this instrument is satisfactory.

The high reliability and robustness, simple use, fast measurement speed of ~ 1 s
as well as high precision (1–2 ppbv at 1 s) and accuracy make this device particularly
suitable for the use on board aircraft. Other commercially available techniques using
gas chromatography and NDIR cannot compete with its measurement speed. Custom-
made systems applying e.g., TDLAS in the mid-infrared (Sachse et al., 1987; Wienhold
et al., 1998) do show a comparable performance, but are much more complex and
require skilled personnel for its use. Recently, a CRDS instrument has been reported
to achieve a precision of 0.2 ppbv with 1 s time resolution onboard aircraft accompanied

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by nearly care-free operation (Provencal et al., 2005). To the best of our knowledge we are not aware of any long-term experience with this instrument.

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Table 1. Results of a round robin experiment with EMPA (Switzerland) and NOAA (US). The MPI instrument was calibrated with a standard of 155.8 ± 0.5 ppbv which was referenced to the EMPA standard cylinder CA06490 with 352.5 ppbv CO. The MPI results are reported with expanded uncertainty resulting from the standard deviation of the individual measurements and the uncertainty of the MPI standard.

Cylinder	MPI 2010 (ppb)	EMPA 2008[a] (ppb)	NOAA 2008[b] (ppb)
CA 08179	74.6 ± 0.5	73.0 ± 0.5	72.5 ± 0.5
CA 06529	102.6 ± 0.5	101.9 ± 0.6	101.6 ± 0.7
CA 08161	164.6 ± 0.7	162.3 ± 0.6	161.3 ± 1.1
CA 08136	230.5 ± 0.8	227.5 ± 1.0	224.6 ± 1.5
CC 113562	296.7 ± 1.1	296.2 ± 1.0	294.0 ± 2.0
CA 08193	401.1 ± 1.5	398.5 ± 1.0	395.2 ± 2.7

[a] Analytical precision.
[b] Includes estimate of uncertainty in the scale
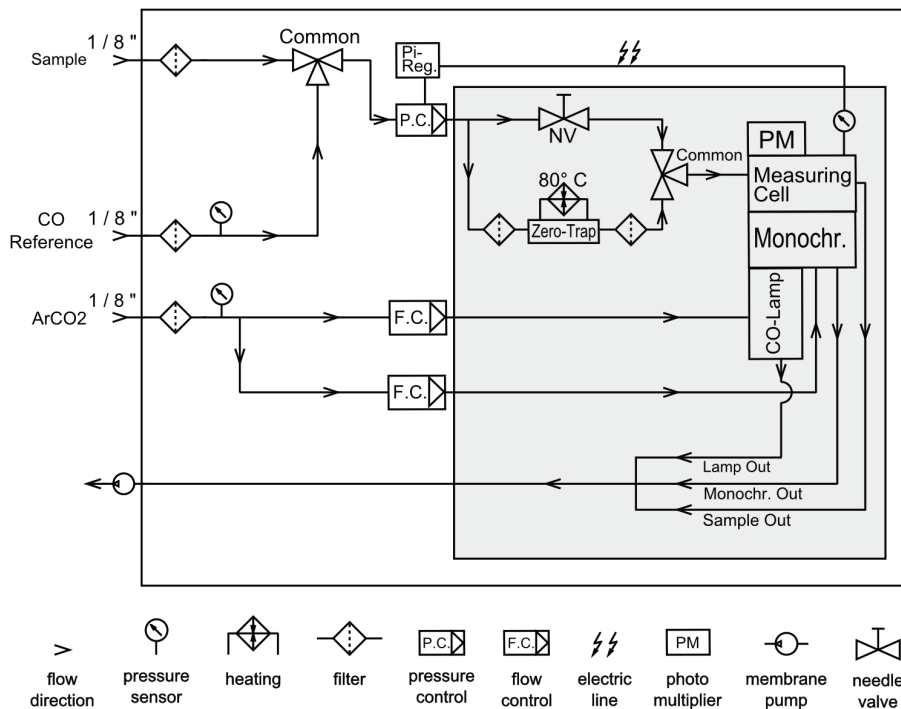
Fig. 1. Flow scheme of the CARIBIC CO instrument. The individual components are described below the sketch.
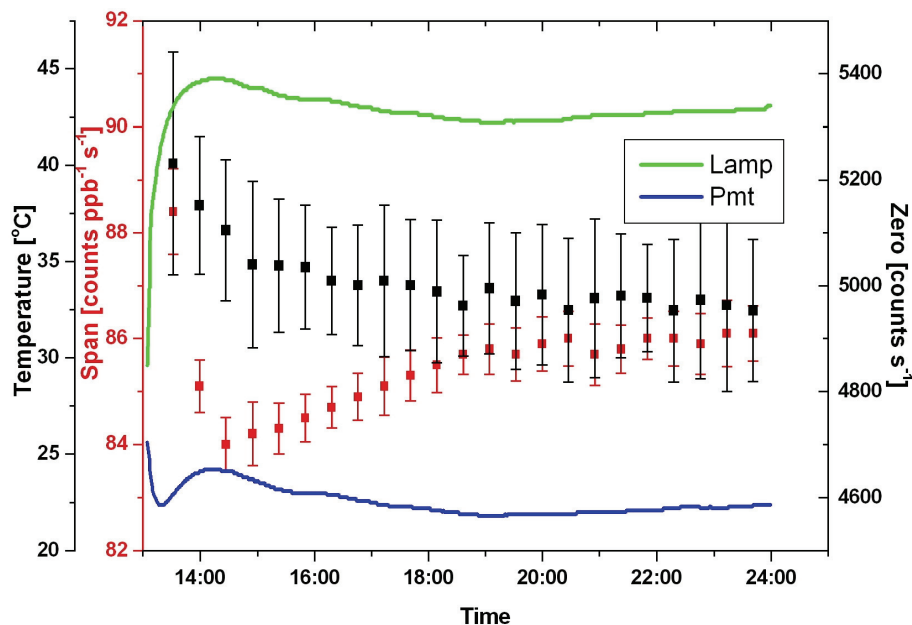
Fig. 2. Sensitivity (red), zero signal (black, right *y*-axis), and temperatures of the photomultiplier (blue) and of the lamp (green) during flight #347 from Frankfurt to Bogotá on 16 June 2011. The temperatures were recorded continuously, while the zero signal and the sensitivity were only measured during the calibration cycles every 25 min. The error bars give the 1σ variation during the last 60 s of each calibration cycle.
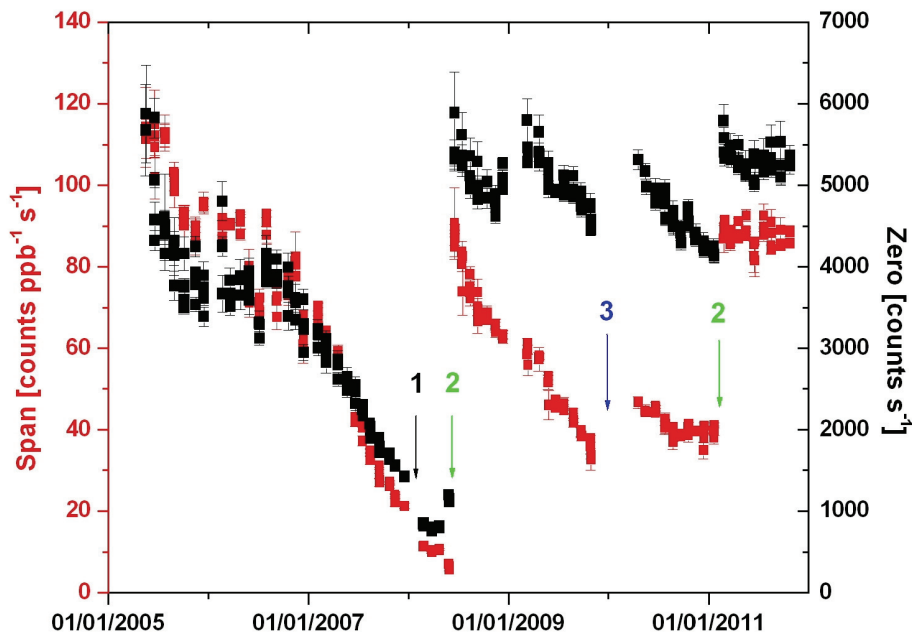
Fig. 3. Long-term progression of the zero signal and the sensitivity during the use onboard the CARIBIC aircraft. The points represent the averages over the duration of each flight (typically of 9–12 h) and the error bars their standard deviation. Instrument maintenance (see text): 1 – replacement of the off-axis parabolic mirror (February 2008), 2 – replacement of the MgF_2 lamp window (June 2008 and February 2011), 3 – switch from N_2 to Ar/CO_2 (December 2009) as a flushing gas for the optics.

CARIBIC flight LH-185
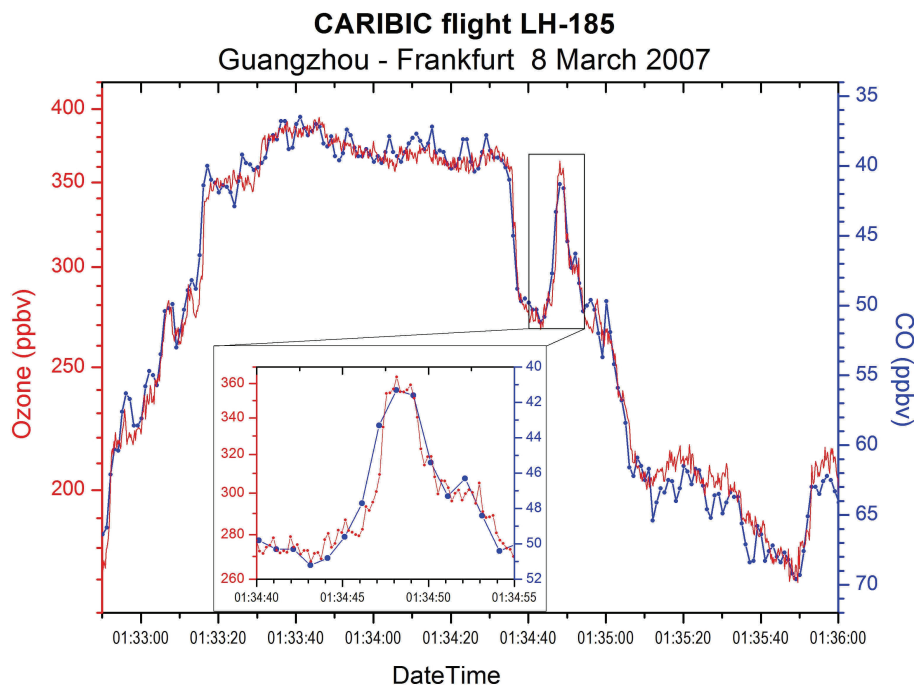Guangzhou - Frankfurt 8 March 2007

Fig. 4. Fast changes of CO and O$_3$ concentrations during a section of flight #185 from Guangzhou to Frankfurt on 8 March 2007. Note the inverse scale for CO. The insert shows a 90 ppbv O$_3$ peak, with a coinciding 8 ppbv drop in CO over a period of only ∼ 12 s (blue dots).