



HAL
open science

An airborne infrared laser spectrometer for in-situ trace gas measurements: application to tropical convection case studies

Valéry Catoire, G. Krysztofiak, Claude Robert, M. Chartier, P. Jacquet, Christophe Guimbaud, Paul D Hamer, V. Marécal

► **To cite this version:**

Valéry Catoire, G. Krysztofiak, Claude Robert, M. Chartier, P. Jacquet, et al.. An airborne infrared laser spectrometer for in-situ trace gas measurements: application to tropical convection case studies. 2022. <insu-03577054>

HAL Id: insu-03577054

<https://insu.hal.science/insu-03577054v1>

Preprint submitted on 16 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons CC BY 4.0 - Attribution - International License



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

An airborne infrared laser spectrometer for in-situ trace gas measurements: application to tropical convection case studies

V. Catoire¹, G. Krysztofiak¹, C. Robert¹, M. Chartier¹, P. Jacquet¹, C. Guimbaud¹, P. D. Hamer^{2,3}, and V. Marécal³

¹LPC2E, Université Orléans – CNRS (UMR 7328), 3A Avenue de la Recherche Scientifique, 45071 Orléans CEDEX 2, France

²CNRM-GAME, Météo-France – CNRS (UMR 3589), 42 Avenue G. Coriolis, 31057 Toulouse CEDEX 1, France

³NILU, P.O. Box 100, 2027 Kjeller, Norway

Received: 28 July 2015 – Accepted: 13 August 2015 – Published: 7 September 2015

Correspondence to: V. Catoire (valery.catoire@cns-orleans.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

A three-channel laser absorption spectrometer called SPIRIT (SPectromètre InfraRouge In situ Toute altitude) has been developed for airborne measurements of trace gases in the troposphere and lower stratosphere. More than three different species can be measured simultaneously with high time resolution (each 1.6 s) using three individual CW-DFB-QCLs (Continuous Wave Distributed FeedBack Quantum Cascade Lasers) coupled to a single Robert multipass optical cell. The lasers are operated in a time-multiplexed mode. Absorption of the mid-infrared radiations occur in the cell (2.8 L with effective path lengths of 134 to 151 m) at reduced pressure, with detection achieved using a HgCdTe detector cooled by Stirling cycle. The performances of the instrument are described, in particular precisions of 1, 1 and 3 %, and volume mixing ratio (vmr) sensitivities of 0.4, 6 and 2.4 ppbv are determined at 1.6 s for CO, CH₄ and N₂O, respectively (at 1 σ confidence level). Estimated accuracies without calibration are about 6 %. Dynamic measuring ranges of about four decades are established. The first deployment of SPIRIT was realized aboard the Falcon-20 research aircraft operated by DLR (Deutsches Zentrum für Luft- und Raumfahrt) within the frame of the SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere) European project in November-December 2011 over Malaysia. The convective outflows from two large convective systems near Borneo Island (6.0° N–115.5° E and 5.5° N–118.5° E) were sampled above 11 km in altitude on 19 November and 9 December, respectively. Correlated enhancements in CO and CH₄ vmr were detected when the aircraft crossed the outflow anvil of both systems. These enhancements were interpreted as the fingerprint of transport from the boundary layer up through the convective system and then horizontal advection in the outflow. Using these observations, the fraction of boundary layer air contained in fresh convective outflow was calculated to range between 22 and 31 %, showing the variability of the mixing taking place during convective transport.

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Infrared (IR) absorption spectroscopy is among the fastest on-line measurement methods of atmospheric trace gases. Using lasers leads to ultra-high spectral resolution ($< 10^{-3} \text{ cm}^{-1}$), and therefore larger sensitivity and selectivity than lower resolution IR method such as Fourier Transform IR (FTIR) spectroscopy. A tunable laser spectrometer essentially consists of one or several laser sources, an optical cell where the trace gas is sampled, a photodetector and the electronic system controlling the laser(s) and the data acquisition. This leads to a very compact instrument with high frequency (in a few seconds or less) and accurate measurements. In principle the laser is tuned over a spectral micro-domain ($< 1 \text{ cm}^{-1}$) to match wavenumbers $\tilde{\nu}_0$ of the ro-vibrational lines of the molecules in question. In order to perform ultra-high resolution spectroscopy, the pressure of the analysed air is reduced to $\sim 10\text{--}50 \text{ hPa}$ in a closed cell. The Beer–Lambert law relationship, Eq. (1), provides quantitative results relevant to atmospheric studies, i.e. volume mixing ratios (vmr; unitless), based on spectroscopic molecular parameters and measured quantities:

$$\text{vmr} = \frac{-10^6 k_B T \ln(I(\tilde{\nu})/I^\circ(\tilde{\nu}))}{\rho L S g(\tilde{\nu} - \tilde{\nu}_0)} \quad (1)$$

where k_B is the Boltzmann constant (units of JK^{-1}), T is the temperature (K), $I(\tilde{\nu})/I^\circ(\tilde{\nu})$ is the transmission at a particular wavenumber $\tilde{\nu}$, ρ is the total pressure (Pa) of the cell containing the sampled molecules, L is the optical path length (cm), S is the line intensity (cm molecule^{-1}) of the molecule depending on the partition functions, the temperature and the lower-state energy E'' of the transition, and $g(\tilde{\nu} - \tilde{\nu}_0)$ is the normalized line profile (cm) at $\tilde{\nu}$ around the wavenumber of the transition line $\tilde{\nu}_0$, most frequently assumed to be a Voigt one in the HITRAN spectroscopic database (Rothman et al., 2013). The Voigt profile is the convolution of the Doppler (Gaussian) profile (with T and molecular mass dependencies) and of the collisional (Lorentzian) profile depending on the pressure ρ , the air-broadened half-width γ_{air} , and the temperature T with

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



dow. An optical multiplexor allows for collecting toward a single exit the three beams which then go out to a BaF₂ beam splitter (BS), dividing them in two parts. A minor part is reflected toward a home-made Fabry-Pérot interferometer etalon used as reference channel for relative wavenumber calibration. A small optical reference cell containing known gaseous species can be added on a second path of this channel for retrieving absolute wavenumber scale. This beam is then focused onto a photovoltaic HgCdTe detector (Judson J19D10) by a spherical mirror. The major part of the beam is directed and focused at the entrance of the multipass optical cell through a BaF₂ window. The measurement output beam also goes through a second BaF₂ window and is then collected by a flat mirror and focused onto an analogous detector by a spherical mirror similar to the reference beam. Both detectors are cooled by the same Stirling cycle cooler (RM2 Thalès Cyrogénie) mounted in a home-made Dewar in which vacuum is maintained by passive pumping using high porosity sintered materials (CapaciTorr[®] D 100 Saes Getters). The detected electrical signals are amplified first by pre-amplifiers with a fixed gain and secondly by an automatically self-adjusted gain in the main electronic module, and digitized by a 16-bit analog-to-digital converter.

The optical cell is a patented multiple-reflection cell detailed in a previous paper (Robert, 2007). In brief, this cell is composed of three mirrors combining the design of the Herriott and White cells, which results in very easy and stable operating conditions and allows for very long optical paths, i.e. 151.00 m (233 reflections) or 134.22 m (207 reflections) in the present experiments, in a compact volume (2.77 L for a cylinder of 3.7 cm radius and 64.5 cm length). This cell is controlled by two high-performance piezoelectric actuators (Newport PZA12) located at each of its ends, shown in Fig. 3 (in orange colour), allowing optical alignment at the desired path number and also the change in the path number by tilting the two mirrors relative to each other. A third actuator (not visible in Fig. 3) is used to move slowly (0.3 Hz) back and forth the stand-alone mirror on a small range, efficiently attenuating the optical interference fringes. The cell temperature is measured by a Pt100 resistance probe with a precision of 0.01 K, and is estimated to be accurate and homogeneous in the cell within 0.5 K, leading to 0.2 %

2.2 Data retrieval

The data retrieval is based on Beer–Lambert law, Eq. (1). As previously explained in detail (Guimbaud et al., 2011; Moreau et al., 2005), it consists in fitting the numerical second derivative of the experimental transmission $I(\tilde{\nu})/I^\circ(\tilde{\nu})$ to that of the simulated transmission, $\exp[-L \cdot S \cdot g(\tilde{\nu} - \tilde{\nu}_0) \cdot C]$, at each wavenumber $\tilde{\nu}$ of the spectral micro-window by adjusting the molecular concentration C (molecules cm^{-3}). The selected micro-windows were usually $2179.70\text{--}2179.85 \text{ cm}^{-1}$, $1249.56\text{--}1249.73 \text{ cm}^{-1}$, and $2064.30\text{--}2064.55 \text{ cm}^{-1}$ for CO , CH_4 and N_2O , and CO_2 , respectively. A linear least-squares algorithm minimizes the residual, i.e. the difference between the experimental and simulated signal. The volume mixing ratio vmr is subsequently deduced from C by knowing the total pressure p and the temperature T of the optical cell. The second derivative method has the advantage of not needing the accurate reconstruction of the 100 % transmission baseline (the continuous component of the signal) where the molecules absorb, and of reducing the optical interference fringes. Both methods give similar results in the present case for which the maximum optical absorptions ($1 - I(\tilde{\nu}_0)/I^\circ(\tilde{\nu}_0)$) are significant, typically 4 % for ~ 100 ppbv CO , 4 % for 1.8 ppmv CH_4 , 1 % for 325 ppbv N_2O and 7 % for 400 ppmv CO_2 . The second derivative method is especially more effective in the case of low absorption (Moreau et al., 2005). Figures 4 A, B, C show examples of spectra for CO , CH_4 , N_2O recorded during one of the two case studies, on the 9 December 2011, and for CO_2 during a transfer flight to Malaysia, on the 8 November 2011. Statistical errors represented by the root mean square noise at 1σ confidence level on the fitting retrievals are indicated in Fig. 4. They are typical of the measurements during this campaign, which were on average 1 % for CO , 1 % for CH_4 , 3 % for N_2O and 1 % for CO_2 .

Due to a failure of the air conditioning system of the aircraft from the first flight during the campaign (16 November), the QCL corresponding to CO_2 measurement could not be maintained at -20.5°C and broke down. Consequently the whole campaign

AMTD

8, 9165–9207, 2015

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1.3 ppbv (0.8‰) for CH₄, 0.8 ppbv for N₂O (3‰) and 0.3 ppmv (0.7‰) for CO₂. The intermediate values at 10 s are noted since this is the typical response time in flight. It is thus expected to detect (1σ_A) variations higher than 0.2 ppbv for CO, 4 ppbv for CH₄ and 2 ppbv for N₂O in flight. The lower performance for N₂O is due to lower optical absorption and thus lower signal-to-noise ratio (improvement can be realised by just changing the spectral domain or the QCL for a larger line intensity). For averages of more than 100 s, it is clearly seen that the deviations increase, though remaining below the precision obtained for 1.6 s averaging. Of course in-flight instantaneous 1σ precisions determined by the spectral fitting error in the previous Sect. 2.2 (1 ppbv for CO, 18 ppbv for CH₄ and 10 ppbv for N₂O) are somewhat greater than the 1σ_A sensitivities at 1.6 s (0.4 ppbv for CO, 6 ppbv for CH₄ and 2.4 ppbv for N₂O) deduced from the statistical distribution of 228 measurements (365 s) because fitting errors include some permanent pattern due to, for instance, Fabry-Perot interference fringes and differences between experimental and simulated line profiles.

For the gas concentrations studied here, the total, without calibration, uncertainty is largely due to the accuracy with which the spectroscopic parameters are known. For the absorption lines used in SPIRIT, the HITRAN database (Rothman et al., 2013) provides line intensities S and air-broadened half-widths γ_{air} , with an accuracy of better than 5%, affecting the vmr accuracy on the same order for the former and two times less for the latter (2.5%); other uncertainties on spectroscopic parameter have negligible impacts (Guimbaud et al., 2011). Taking into account other uncertainty sources (0.3% on pressure and 0.2% on temperature: see above Sect. 2.1; and the retrieval fitting errors), the estimated accuracies calculated as the square root of the quadratic sum are 5.7% for CO and CH₄ and 6.4% for N₂O. Since the most influent parameter, i.e. the line intensity, is an intrinsic value of the molecules, it does not vary with the measurement conditions and can result in a constant bias on vmr estimation. In order to determine this bias, more than 850 measurements of a calibrated gas have been performed. The cylinder containing this gas mixture (Scott-Marrin Inc.) had been calibrated by the WMO GAW Central Calibration Laboratories: 102.1 ± 0.7 ppbv CO, 1822 ± 3 ppbv

ber 2011 are presented. The flight on the 19 November began from Miri at 07:50 UTC (15:50 local time), flew North along the coast towards Kota Kinabalu, and ended at Miri at 10:10 UTC (18:10 local time). The flight on the 9 December took place between Tawau and Miri over Borneo between 08:15 UTC (16:15 local time) and 10:50 UTC (18:50 local time). The CO vmr decreased with increasing altitude from 120–150 ppbv near the ground (> 1 km) to 70–80 ppbv in the free troposphere (8–10 km).

3.2 In-situ measurements of CO and CH₄ for the study of transport by deep convection

3.2.1 Meteorological situations of the flights

One of the objectives of the SHIVA field campaign was to study the pathways of halogen VSLs emitted from the oceans in the boundary layer to the upper troposphere and then to the lower stratosphere, and to quantify these transport processes. The main mechanism leading to a rapid transport of air from the lower troposphere to the upper troposphere in the tropics is deep convection. This is why the SHIVA field campaign took place during the early winter monsoon season. During the campaign, several Falcon aircraft flights were conducted around 11–13 km in altitude, in order to sample the upper troposphere in the vicinity of deep tropical convection. To highlight the application of the SPIRIT measurements for characterising the air composition in the upper troposphere, we studied the two flight measurements around 12 km altitude within the outflow of deep convective systems, as presented above (Sect. 3.1). Figures 9 and 10 depict the flight tracks over-plotted, respectively, on the brightness temperatures from the 11 μm channel IR108 on board the Japanese geostationary multifunctional transport satellite MTSAT-2 and the corresponding cloud height estimation based on Hamada and Nishi (2010) http://database.rish.kyoto-u.ac.jp/arch/ctop/index_e.html. Brightness temperature represents thermal radiative intensity emitted by the cloud top and is used for the detection of convective activity (Iwasaki et al., 2010); this temperature decreases with increasing cloud height.

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Berman, E. S. F., Fladeland, M., Liem, J., Kolyer, R., and Gupta, M.: Greenhouse gas analyser for measurements of carbon dioxide, methane, and water vapor aboard an unmanned aerial vehicle, *Sensor Actuat. B-Chem.*, 169, 128–135, doi:10.1016/j.snb.2012.04.036, 2012.
- Bertram, T. H., Perring, A. E., Wooldridge, P. J., Crouse, J. D., Kwan, A. J., Wennberg, P. O., Scheuer, E., Dibb, J., Avery, M., Sachse, G., Vay, S. A., Crawford, J. H., McNaughton, C. S., Clarke, A., Pickering, K. E., Fuelberg, H., Huey, G., Blake, D. R., Singh, H. B., Hall, S. R., Shetter, R. E., Fried, A., Heikes, B. G., and Cohen, R. C.: Direct measurements of the convective recycling of the upper troposphere, *Science*, 315, 816–820, 2007.
- Borbon, A., Ruiz, M., Bechara, J., Aumont, B., Chong, M., Huntrieser, H., Mari, C., Reeves, C. E., Scialom, G., Hamburger, T., Stark, H., Afif, C., Jambert, C., Mills, G., Schlager, H., and Perros, P. E.: Transport and chemistry of formaldehyde by mesoscale convective systems in West Africa during AMMA 2006, *J. Geophys. Res.*, 117, D12301, doi:10.1029/2011JD017121, 2012.
- Christensen, L. E., Webster, C. R., and Yang, R. Q.: Aircraft and balloon in situ measurements of methane and hydrochloric acid using interband cascade lasers, *Appl. Opt.*, 46, 1132–1138, 2007.
- Cohan, D. S., Schultz, M. G., Jacob, D. J., Heikes, B. G., and Blake, D. R.: Convective injection and photochemical decay of peroxides in the tropical upper troposphere: methyl iodide as a tracer of marine convection, *J. Geophys. Res.*, 104, 5717–5724, 1999.
- Curl, R. F., Capasso, F., Gmachl, C., Kosterev, A. A., McManus, B., Lewicki, R., Pusharsky, M., Wysocki, G., and Tittel, F. K.: Quantum cascade lasers in chemical physics, *Chem. Phys. Lett.*, 487, 1–18, 2010.
- D'Amato, F., Mazzinghi, P., and Castagnoli, F.: Methane analyzer based on TDL for measurements in the lower stratosphere: design and laboratory tests, *Appl. Phys. B*, 75, 195–202, 2002.
- de Reus, M., Fischer, H., Arnold, F., de Gouw, J., Holzinger, R., Warneke, C, and Williams, J.: On the relationship between acetone and carbon monoxide in different air masses, *Atmos. Chem. Phys.*, 3, 1709–1723, doi:10.5194/acp-3-1709-2003, 2003.
- Durry, G., Amarouche, N., Joly, L., Liu, X., Parvite, B., and Zéninari, V.: Laser diode spectroscopy of H₂O at 2.63 μm for atmospheric applications, *Appl. Phys. B*, 90, 573–580, doi:10.1007/s00340-007-2884-3, 2007.
- Dyroff, C., Zahn, A., Sanati, S., Christner, E., Rauthe-Schöch, A., and Schuck, T. J.: Tunable diode laser in-situ CH₄ measurements aboard the CARIBIC passenger aircraft: instrument

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

performance assessment, *Atmos. Meas. Tech.*, 7, 743–755, doi:10.5194/amt-7-743-2014, 2014.

Dyroff, C., Sanati, S., Christner, E., Zahn, A., Balzer, M., Bouquet, H., McManus, J. B., González-Ramos, Y., and Schneider, M.: Airborne in situ vertical profiling of HDO/H₂¹⁶O in the subtropical troposphere during the MUSICA remote sensing validation campaign, *Atmos. Meas. Tech.*, 8, 2037–2049, doi:10.5194/amt-8-2037-2015, 2015.

Fried, A. and Richter, D.: Infrared absorption spectroscopy, in: *Analytical Techniques for Atmospheric Measurement*, edited by: Heard, D., Blackwell Publishing Ltd., Oxford, UK, 72–146, 2006.

Fried, A., Wert, B., Henry, B. E., and Drummond, J. R.: Airborne tunable diode laser measurements of formaldehyde, *Spectrochim. Acta A-M.*, 55, 2097–2110, doi:10.1016/S1386-1425(99)00082-7, 1999.

Fried, A., Wang, Y., Cantrell, C., Wert, B., Walega, W., Ridley, B., Atlas, E., Shetter, R., Lefer, B., Coffey, M.T., Hannigan, J., Blake, D., Blake, N., Meinardi, S., Talbot, B., Dibb, J., Scheuer, E., Wingenter, O., Snow, J., Heikes, B., and Ehhalt, D.: Tunable diode laser measurements of formaldehyde during the TOPSE 2000 study: distributions, trends, and model comparisons, *J. Geophys. Res.*, 108, 8365, doi:10.1029/2002JD002208, 2003.

Gheusi, F., Ravetta, F., Delbarre, H., Tsamalis, C., Chevalier-Rosso, A., Leroy, C., Augustin, P., Delmas, R., Ancellet, G., Athier, G., Bouchou, P., Campistron, B., Cousin, J.-M., Fourmentin, M., and Meyerfeld, Y.: Pic 2005, a field campaign to investigate low-tropospheric ozone variability in the Pyrenees, *Atmos. Res.*, 101, 640–665, doi:10.1016/j.atmosres.2011.04.014, 2011.

Gogo, S., Guimbaud, C., Laggoun-Défarge, F., Catoire, V., and Robert, C.: In situ quantification of CH₄ bubbling events from a peat soil using a new infrared laser spectrometer, *J. Soils Sediments*, 11, 545–551, doi:10.1007/s11368-011-0338-3, 2011.

Guimbaud, C., Catoire, V., Gogo, S., Robert, C., Laggoun-Défarge, F., Chartier, M., Grossel, A., Albéric, P., Pomathiod, L., Nicoullaud, B., and Richard, G.: A portable infrared laser spectrometer for flux measurements of trace gases at the geosphere-atmosphere interface, *Meas. Sci. Technol.*, 22, 075601, doi:10.1088/0957-0233/22/7/075601, 2011.

Hamada, A. and Nishi, N.: Development of a cloud-top height estimation method by geostationary satellite split-window measurements trained with CloudSat data, *J. Appl. Meteor. Climate*, 49, 2035–2049, 2010.

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Hamer, P. D., Marécal, V., Hossaini, R., Pirre, M., Warwick, N., Chipperfield, M., Samah, A. A., Harris, N., Robinson, A., Quack, B., Engel, A., Krüger, K., Atlas, E., Subramaniam, K., Oram, D., Leedham, E., Mills, G., Pfeilsticker, K., Sala, S., Keber, T., Bönisch, H., Peng, L. K., Nadzir, M. S. M., Lim, P. T., Mujahid, A., Anton, A., Schlager, H., Catoire, V., Krysztofiak, G., Fühlbrügge, S., Dorf, M., and Sturges, W. T.: Modelling the chemistry and transport of bromoform within a sea breeze driven convective system during the SHIVA Campaign, *Atmos. Chem. Phys. Discuss.*, 13, 20611–20676, doi:10.5194/acpd-13-20611-2013, 2013.
- Herndon, S. C., Zahniser, M. S., Nelson Jr., D. D., Shorter, J., McManus, J. B., Jimenez, R., Warneke, C., and de Gouw, J. A.: Airborne measurements of HCHO and HCOOH during the New England Air Quality Study 2004 using a pulsed quantum cascade laser spectrometer, *J. Geophys. Res.*, 112, D10S03, doi:10.1029/2006JD007600, 2007.
- Iwasaki, S., Shibata, T., Nakamoto, J., Okamoto, H., Ishimoto, H., and Kubota, H.: Characteristics of deep convection measured by using the A-train constellation, *J. Geophys. Res.*, 115, D06207, doi:10.1029/2009JD013000, 2010.
- Kerstel, E. R. T., Iannone, R. Q., Chenevier, M., Kassi, S., Jost, H.-J., and Romanini, D.: A water isotope (^2H , ^{17}O , and ^{18}O) spectrometer based on optical feedback cavity-enhanced absorption for in situ airborne applications, *Appl. Phys. B*, 85, 397–406, 2006.
- Kormann, R., Fischer, H., de Reus, M., Lawrence, M., Brühl, Ch., von Kuhlmann, R., Holzinger, R., Williams, J., Lelieveld, J., Warneke, C., de Gouw, J., Heland, J., Ziereis, H., and Schlager, H.: Formaldehyde over the eastern Mediterranean during MINOS: Comparison of airborne in-situ measurements with 3D-model results, *Atmos. Chem. Phys.*, 3, 851–861, doi:10.5194/acp-3-851-2003, 2003.
- Kort, E. A., Patra, P. K., Ishijima, K., Daube, B. C., Jiménez, R., Elkins, J., Hurst, D., Moore, F. L., Sweeney, C., and Wofsy, S. C.: Tropospheric distribution and variability of N_2O : evidence for strong tropical emissions, *Geophys. Res. Lett.*, 38, L15806, doi:10.1029/2011GL047612, 2011.
- Lopez, J. P., Luo, M., Christensen, L. E., Loewenstein, M., Jost, H., Webster, C. R., and Osterman, G.: TES carbon monoxide validation during two AVE campaigns using the Argus and ALIAS instruments on NASA's WB-57F, *J. Geophys. Res.*, 113, D16S47, doi:10.1029/2007JD008811, 2008.
- Marandino, C. A., Tegtmeier, S., Krüger, K., Zindler, C., Atlas, E. L., Moore, F., and Bange, H. W.: Dimethylsulphide (DMS) emissions from the western Pacific Ocean: a potential marine

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

source for stratospheric sulphur?, *Atmos. Chem. Phys.*, 13, 8427–8437, doi:10.5194/acp-13-8427-2013, 2013.

McManus, J. B., Nelson, D. D., Shorter, J. H., Jimenez, R., Herndon, S., Saleska, S., and Zahniser, M.: A high precision pulsed quantum cascade laser spectrometer for measurements of stable isotopes of carbon dioxide, *J. Mod. Opt.*, 52, 2309–2321, 2005.

McManus, J. B., Zahniser, M. S., and Nelson, D. D.: Dual quantum cascade laser trace gas instrument with astigmatic Herriott cell at high pass number, *Appl. Optics*, 50, A74–A85, 2011.

McQuaid, J., Schlager, H., Andrés-Hernández, M. D., Ball, S., Borbon, A., Brown, S. S., Catoire, V., Di Carlo, P., Custer, T. G., von Hobe, M., Hopkins, J., Pfeilsticker, K., Röckmann, T., Roiger, A., Stroh, F., Williams, J., and Ziereis, H.: Chapter 3: In situ trace gas measurements, in: *Airborne Measurements: Methods and Instruments*, edited by: Wendisch, M. and Brenguier, J.-L., EUFAR Wiley-VCH, Weinheim (Germany), 104–107, 2013.

Moreau, G., Robert, C., Catoire, V., Chartier, M., Camy-Peyret, C., Huret, N., Pirre, M., Pomathiod, L., and Chalumeau, G.: SPIRALE: a multispecies in situ balloon-borne experiment with six tunable diode laser spectrometers, *Appl. Optics*, 44, 5972–5989, 2005.

Neuman, J. A., Huey, L. G., Ryerson, T. B., and Fahey, D. W.: Study of inlet materials for sampling atmospheric nitric acid, *Environ. Sci. Technol.*, 33, 1133–1136, 1999.

Podolske, J. R., Sachse, G. W., and Diskin, G. S.: Calibration and data retrieval algorithms for the NASA Langley/Ames Diode Laser Hygrometer for the NASA transport and chemical evolution over the Pacific (TRACE-P) mission, *J. Geophys. Res.*, 108, 8792, doi:10.1029/2002JD003156, 2003.

Ray, E. A., Rosenlof, K. H., Richard, E. C., Hudson, P. K., Cziczo, D. J., Loewenstein, M., Jost, H.-J., Lopez, J., Ridley, B., Weinheimer, A., Montzka, D., Knapp, D., Wofsy, S. C., Daube, B. C., Gerbig, C., Xueref, I., and Herman, R. L.: Evidence of the effect of summertime midlatitude convection on the subtropical lower stratosphere from CRYSTAL-FACE tracer measurements, *J. Geophys. Res.*, 109, D18304, doi:10.1029/2004JD004655, 2004.

Robert, C.: Simple, stable, and compact multiple-reflection optical cell for very long optical paths, *Appl. Optics*, 46, 5408–5418, 2007.

Rollins, A. W., Thornberry, T. D., Gao, R. S., Smith, J. B., Sayres, D. S., Sargent, M. R., Schiller, C., Krämer, M., Spelten, N., Hurst, D. F., Jordan, A. F., Hall, E. G., Vömel, H., Diskin, G. S., Podolske, J. R., Christensen, L. E., Rosenlof, K. H., Jensen, E. J., and Fahey, D. W.:

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Evaluation of UT/LS hygrometer accuracy by intercomparison during the NASA MACPEX mission, *J. Geophys. Res. Atmos.*, 119, 1915–1935, doi:10.1002/2013JD020817, 2014.

Rothman, L. S., Gordon, I. E., Babikov, Y., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M., Bizzocchi, L., Boudon, V., Brown, L. R., Campargue, A., Chance, K., Cohen, E. A., Coudert, L. H., Devi, V. M., Drouin, B. J., Fayt, A., Flaud, J.-M., Gamache, R. R., Harrison, J. J., Hartmann, J.-M., Hill, C., Hodges, J. T., Jacquemart, D., Jolly, A., Lamouroux, J., LeRoy, R. J., Li, G., Long, D. A., Lyulin, O. M., Mackie, C. J., Massie, S. T., Mikhailenko, S., Müller, H. S. P., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E. R., Richard, C., Smith, M. A. H., Starikova, E., Sung, K., Tashkun, S., Tennyson, J., Toon, G. C., Tyuterev, V. G., and Wagner, G.: The HITRAN2012 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, 130, 4–50, 2013.

Santoni, G. W., Daube, B. C., Kort, E. A., Jiménez, R., Park, S., Pittman, J. V., Gottlieb, E., Xiang, B., Zahniser, M. S., Nelson, D. D., McManus, J. B., Peischl, J., Ryerson, T. B., Holloway, J. S., Andrews, A. E., Sweeney, C., Hall, B., Hints, E. J., Moore, F. L., Elkins, J. W., Hurst, D. F., Stephens, B. B., Bent, J., and Wofsy, S. C.: Evaluation of the airborne quantum cascade laser spectrometer (QCLS) measurements of the carbon and greenhouse gas suite – CO₂, CH₄, N₂O, and CO – during the CalNex and HIPPO campaigns, *Atmos. Meas. Tech.*, 7, 1509–1526, doi:10.5194/amt-7-1509-2014, 2014.

Scott, D. C., Herman, R. L., Webster, C. R., May, R. D., Flesch, G. J., and Moyer, E. J.: Airborne Laser Infrared Absorption Spectrometer (ALIAS-II) for in situ atmospheric measurements of N₂O, CH₄, CO, HCl, and NO₂ from balloon or remotely piloted aircraft platforms, *Appl. Optics*, 38, 4609–4622, 1999.

Spiers, G. D., Menzies, R. T., Jacob, J., Christensen, L. E., Phillips, M. W., Choi, Y. H., and Browell, E. V.: Atmospheric CO₂ measurements with a 2 μm airborne laser absorption spectrometer employing coherent detection, *Appl. Opt.*, 50, 2098–2111, doi:10.1364/AO.50.002098, 2011.

Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Blake, D. R., Boenisch, H., Engel, A., Hepach, H., Hossaini, R., Navarro, M. A., Raimund, S., Sala, S., Shi, Q., and Ziska, F.: The contribution of oceanic methyl iodide to stratospheric iodine, *Atmos. Chem. Phys.*, 13, 11869–11886, doi:10.5194/acp-13-11869-2013, 2013.

Viciani, S., D'Amato, F., Mazzinghi, P., Castagnoli, F., Toci, G., and Werle, P.: A cryogenically operated laser diode spectrometer for airborne measurement of stratospheric trace gases, *Appl. Phys. B*, 90, 581–592, doi:10.1007/s00340-007-2885-2, 2008.

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Wecht, K. J., Jacob, D. J., Wofsy, S. C., Kort, E. A., Worden, J. R., Kulawik, S. S., Henze, D. K., Kopacz, M., and Payne, V. H.: Validation of TES methane with HIPPO aircraft observations: implications for inverse modeling of methane sources, *Atmos. Chem. Phys.*, 12, 1823–1832, doi:10.5194/acp-12-1823-2012, 2012.

5 Wert, B. P., Fried, A., Rauenbuehler, S., Walega, J., and Henry, B.: Design and performance of a tunable diode laser absorption spectrometer for airborne formaldehyde measurements, *J. Geophys. Res.*, 108, 4350, doi:10.1029/2002JD002872, 2003.

10 Wienhold, F. G., Fischer, H., Hoor, P., Wagner, V., Königstedt, R., Harris, G., W., Anders, J., Grisar, R., Knothe, M., Riedel, W. J., Lübken, F.-J., and Schilling, T.: TRISTAR – a tracer in situ TDLAS for atmospheric research, *Appl. Phys. B*, 67, 411–417, doi:10.1007/s003400050524, 1998.

15 Yacovitch, T. I., Herndon, S. C., Roscioli, J. R., Floerchinger, C., McGovern, R. M., Agnese, M., Pétron, G., Kofler, J., Sweeney, C., Karion, A., Conley, S. A., Kort, E. A., Nähle, L., Fischer, M., Hildebrandt, L., Koeth, J., McManus, J. B., Nelson, D. D., Zahniser, M. S. and Kolb, C. E.: Demonstration of an ethane spectrometer for methane source identification, *Environ. Sci. Technol.*, 48, 8028–8034, 2014.

Zondlo, M. A., Paige, M. E., Massick, S. M., and Silver, J. A.: Vertical cavity laser hygrometer for the National Science Foundation Gulfstream-V aircraft, *J. Geophys. Res.*, 115, D20309, doi:10.1029/2010JD014445, 2010.

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Table 1.** Spectral domains and condition emissions of QCLs.

Molecule	Spectral domain (cm ⁻¹)	Current + ramp (mA)	<i>T</i> (°C) of the QCL
CO	2179.6–2179.9	590+20	–12.5
CH ₄ , N ₂ O	1249.4–1249.9	490+23	+16.8
CO ₂	2064.2–2064.7	565+50	–20.5

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Table 2. Performance characteristics for CO, CH₄ and N₂O volume mixing ratio measurements (vmr). Sensitivities and relative accuracies are given for vmr close to typical atmospheric levels (100 ppbv CO, 1.8 ppmv CH₄ and 325 ppbv N₂O).

Mole- cule	1.6 s fitting precision in flight	Lower limit of detection	Sensitivity: $1\sigma_A$ Allan deviation (ppbv) at three different averaging times			Estimated accuracies without calibration	Calculated accuracies after calibration
			1.6 s	10 s	100 s		
CO	1 ppbv (1%)	0.6 ppbv	0.4	0.22	0.13	5.7%	0.9 ppbv (0.9%)
CH ₄	18 ppbv (1%)	9.0 ppbv	6.0	4.0	1.3	5.7%	8.6 ppbv (0.5%)
N ₂ O	10 ppbv (3%)	5.3 ppbv	2.4	2.0	0.8	6.4%	3.8 ppbv (1.2%)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 3. Mean mixing ratios for the boundary layer ($[X]_{\text{surface}}$), upper troposphere ($[X]_{\text{UT}}$) and convective air masses ($[X]_{\text{UTconv}}$) for CO and CH₄ measured by the SPIRIT instrument during the flight on the 19 November and 9 December 2011. These vmr are used in the calculation of the fraction f of air coming from the boundary layer detected in the convective air mass. The mean fraction f found is compared with other convective case studies.

			$[X]_{\text{surface}}$ (ppbv)	$[X]_{\text{UT}}$ (ppbv)	$[X]_{\text{UTconv}}$ (ppbv)	Fraction f ¹	Comment
This study	19 Nov	CO	101	75	81	0.23 ± 0.04	Borneo region
		CH ₄	1901	1871	1879	0.27 ± 0.50	
	9 Dec	CO	130	70	83	0.22 ± 0.05	(6° N–117° E)
		CH ₄	1860	1808	1824	0.31 ± 0.24	
		Mean				0.26 ± 0.05	
Cohan et al. (1999)						0.36–0.68	South Pacific (60° S–10° N)
Ray et al. (2004)						0.20–0.45	Mexico gulf (20° N)
Bertram et al. (2007)						0.17 ± 0.08	East USA and Canada
Bechara et al. (2010)						0.40 ± 0.15	West Africa

¹ Uncertainties are 1σ on the mean.

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

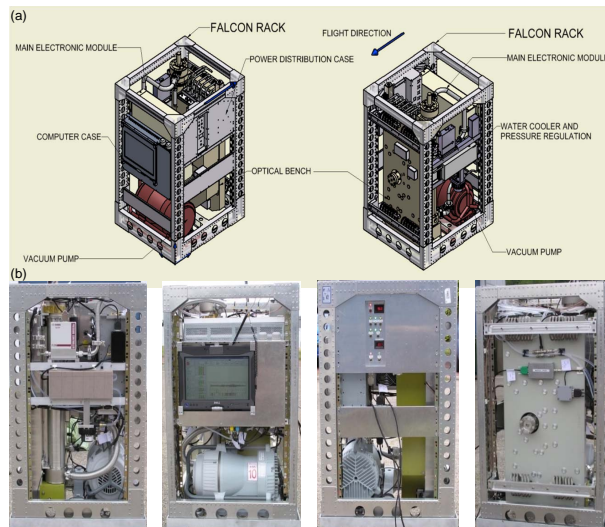


Figure 1. (a) Sketch of the SPIRIT instrument and (b) photographs of its four faces integrated in the Falcon-20 rack.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

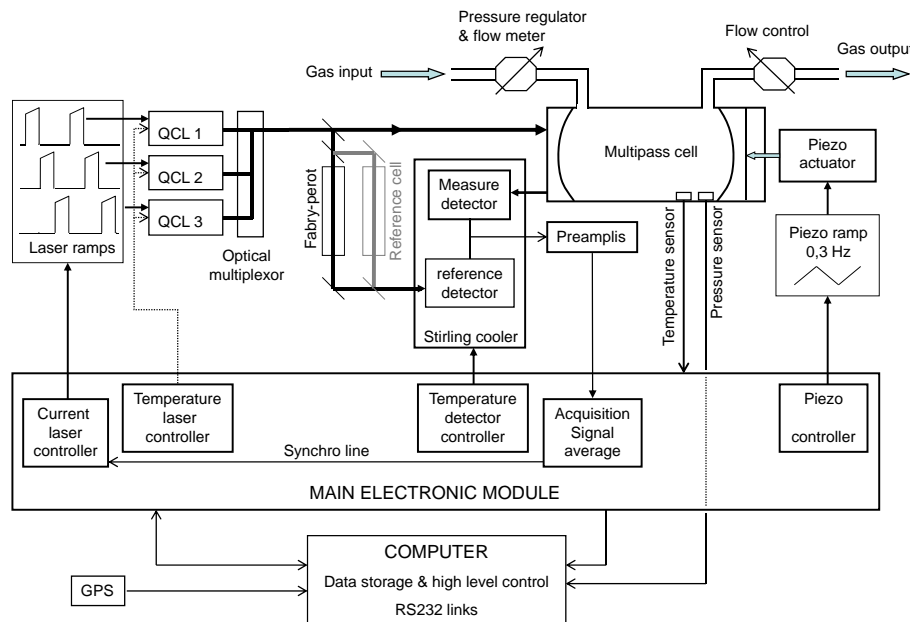


Figure 2. Layout of the functioning principle of the SPIRIT instrument.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

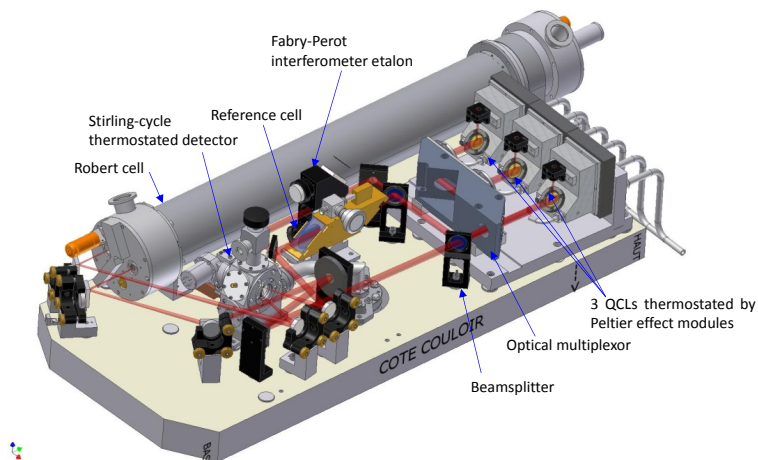


Figure 3. Three-dimensional representation of the optical bench with red rays symbolizing the laser beam paths.

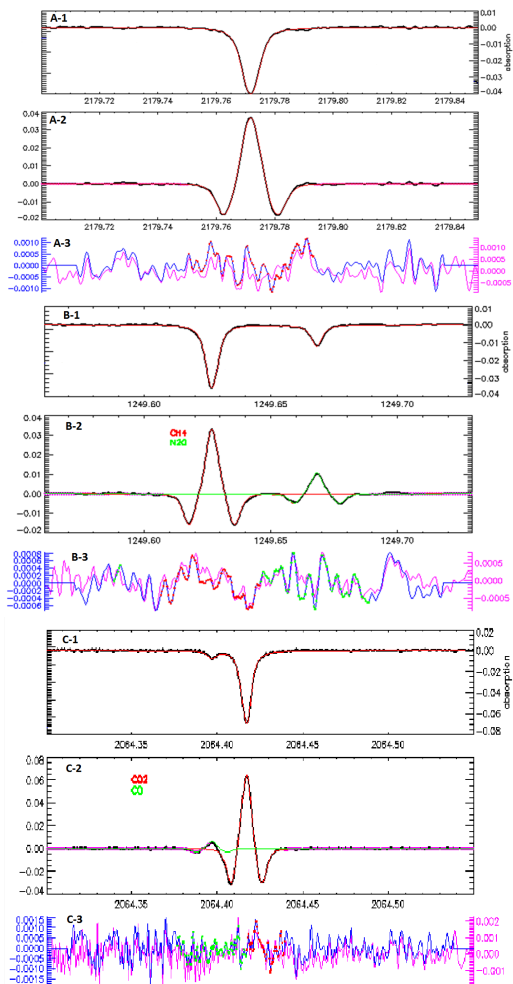
[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

AMTD

8, 9165–9207, 2015

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.



Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

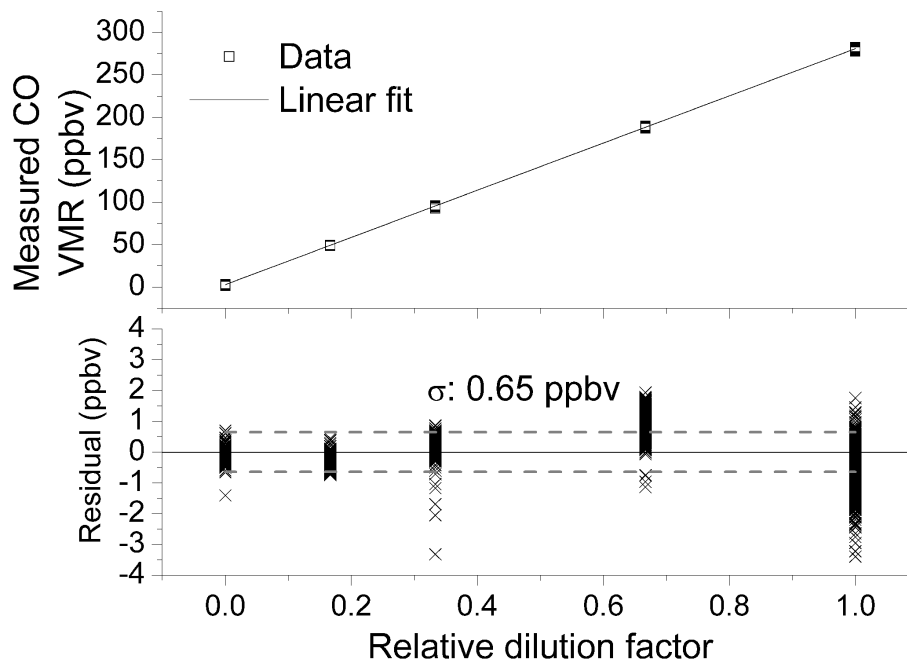


Figure 5. Illustration of linearity of the measurements for CO. Residuals come from subtracting linear fit to data points. Residuals spread around linear fit with one standard deviation $1\sigma = 0.65 \text{ ppbv}$ for 3500 separate data.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

AMTD

8, 9165–9207, 2015

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

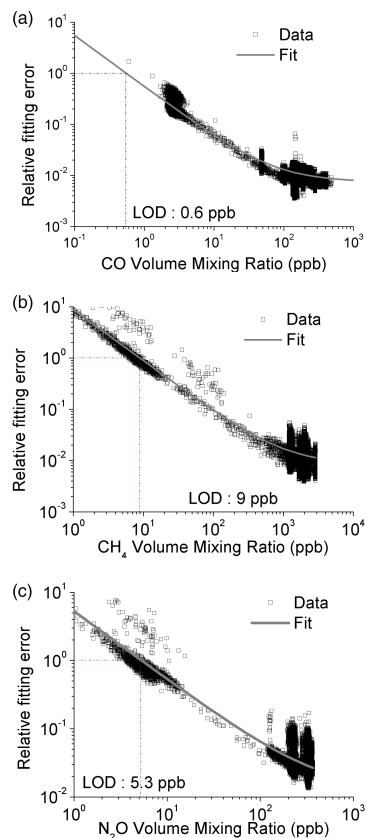


Figure 6. Relative errors on line fittings leading to the total volume mixing ratios (vmr) of CO (a), CH₄ (b) and N₂O (c).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

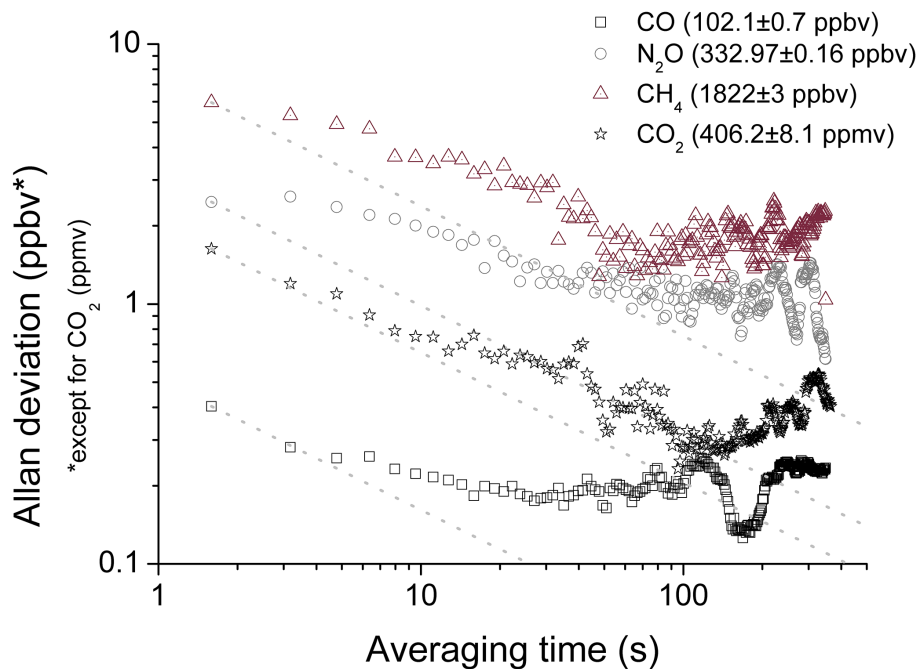


Figure 7. Allan deviation plots showing long term precision and drift behaviour. The expected Allan deviation for an ideal white noise is given as a comparison (dashed lines).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

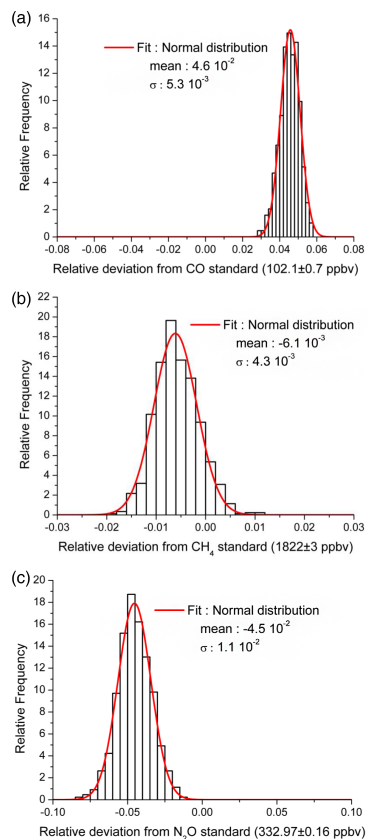


Figure 8. Histograms illustrating measurement dispersion for CO (a), CH₄ (b) and N₂O (c) relatively to standard gas concentrations. The mean values represent the measurement bias and σ the standard deviation for the fitted distribution assumed to be normal (Gaussian). Relative frequencies are normalized to 100 %.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[⏴](#)[⏵](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

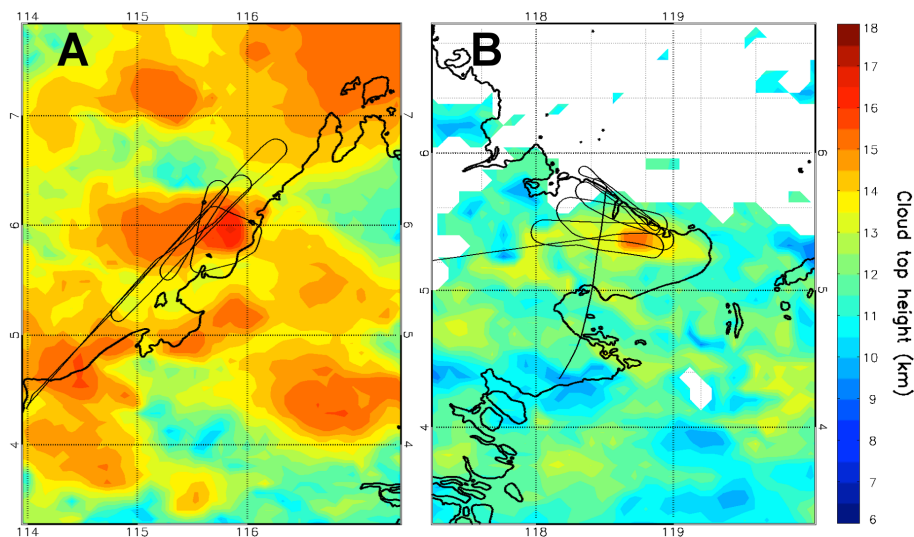


Figure 10. Top cloud height estimate by Hamada and Nishi (2010; available at http://database.rish.kyoto-u.ac.jp/arch/ctop/index_e.html) from the brightness temperature from MTSAT-2 (11–12 μm), obtained at 09:00 UTC on 19 November 2011 **(a)** and 10:00 UTC on 9 December 2011 **(b)**. The flight tracks are represented in dark lines.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

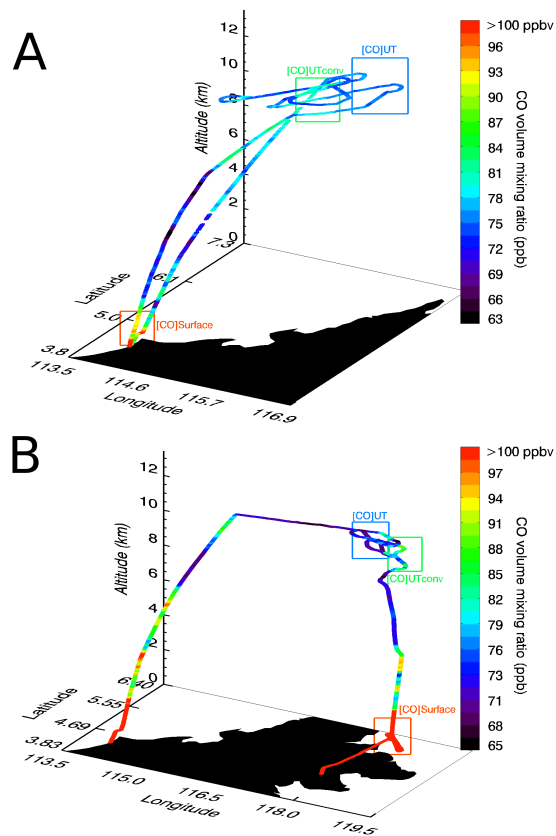


Figure 11. CO volume mixing ratio along the flight trajectories for the flights on 19 November 2011 (a) and on 9 December 2011 (b).

An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An airborne infrared laser spectrometer for in-situ trace gas measurements

V. Catoire et al.

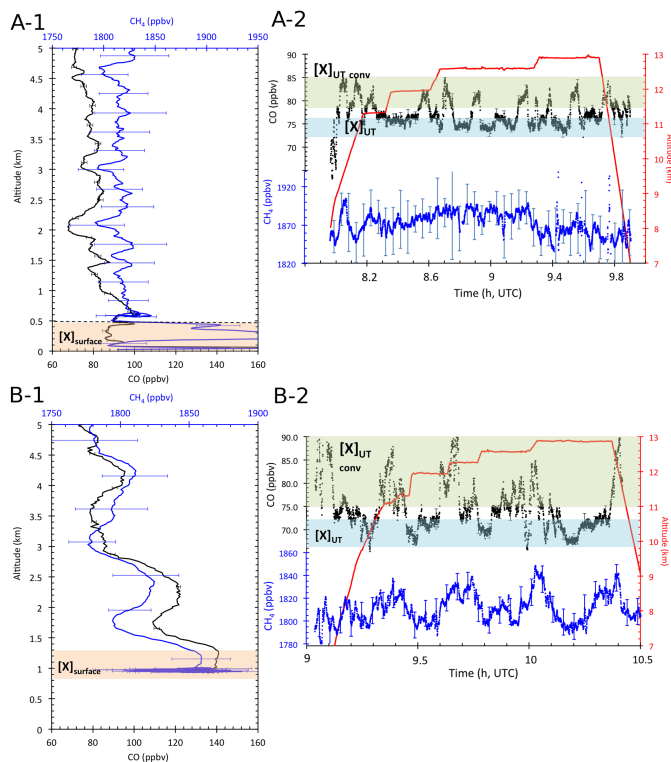


Figure 12. CO (in black) and CH₄ (in blue) volume mixing ratio vs. altitude (**a1**, **b1**) and vs. time (**a2**, **b2**) for the flights on 19 November 2011 (**a**) and on 9 December 2011 (**b**). $[X]_{\text{surface}}$, $[X]_{\text{UT}}$ and $[X]_{\text{UT conv}}$ represent the volume mixing ratios of CO or CH₄ in the boundary layer, in the upper troposphere and in the upper troposphere influenced by the convection, respectively. The vertical profiles of vmr on 19 November and on 9 December are measured during the take-off and the landing of the aircraft and below the convection.