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## An Intercomparison of Ground-based Solar FTIR Measurements of Atmospheric Gases at Eureka, Canada

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## Abstract

We report the results of an intercomparison of vertical column amounts of hydrogen chloride (HCl), hydrogen fluoride (HF), nitrous oxide (N<sub>2</sub>O), nitric acid (HNO<sub>3</sub>), methane (CH<sub>4</sub>), ozone (O<sub>3</sub>), carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) derived from the spectra recorded by two ground-based Fourier transform infrared (FTIR) spectrometers operated side-by-side using the sun as a source. The procedure used to record spectra and derive vertical column amounts follows the format of previous instrument intercomparisons organised by the Network for Detection of Atmospheric Composition Change (NDACC), formerly known as the Network for Detection of Stratospheric Change (NDSC). For most gases the differences were typically around 3% and in about half of the results the error bars given by the standard deviation of the measurements from each instrument did not overlap. The worst level of agreement was for HF where differences of over 5% were typical. The level of agreement achieved during this intercomparison is a little worse than that achieved in previous intercomparisons between ground-based FTIR spectrometers.

## Keywords

Atmospheric, FTIR, spectroscopy, Gases, Remote sensing, Intercomparison

## Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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# An Intercomparison of Ground-based Solar FTIR Measurements of Atmospheric Gases at Eureka, Canada.

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## **Abstract.**

We report the results of an intercomparison of vertical column amounts of hydrogen chloride (HCl), hydrogen fluoride (HF), nitrous oxide (N<sub>2</sub>O), nitric acid (HNO<sub>3</sub>), methane (CH<sub>4</sub>), ozone (O<sub>3</sub>), carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) derived from the spectra recorded by two ground-based Fourier transform infrared (FTIR) spectrometers operated side-by-side using the sun as a source. The procedure used to record spectra and derive vertical column amounts follows the format of previous instrument intercomparisons organised by the Network for Detection of Atmospheric Composition Change (NDACC), formerly known as the Network for Detection of Stratospheric Change (NDSC).

For most gases the differences were typically around 3% and in about half of the results the error bars given by the standard deviation of the measurements from each instrument did not overlap. The worst level of agreement was for HF where differences of over 5% were typical. The level of agreement achieved during this intercomparison is a little worse than that achieved in previous intercomparisons between ground-based FTIR spectrometers.

**Keywords:** Fourier transform, FTIR, intercomparison, atmospheric spectroscopy, trace gases, remote sensing

## 1. Introduction

The Network for Detection of Atmospheric Composition Change (NDACC)(Kurylo 1991) is a global network of ground-based remote sensing stations, using predominantly spectroscopic techniques to measure the chemical composition of the atmosphere. Originally focused on the detection and characterisation of long-term trends in stratospheric ozone and gases involved in ozone chemistry, the NDACC now also provides measurements of predominantly tropospheric trace gases as well as a coordinated resource for comparison and calibration of satellite-borne instruments for atmospheric composition measurements. Further details can be obtained from the NDACC web site, <http://www.ndsc.ncep.noaa.gov> .

In order to ensure the quality of the measurements, the NDACC stipulates a validation protocol (Kurylo 1997) to be followed by all instruments, of which the intercomparison of instruments forms a pivotal role. Previous NDACC FTIR instrument intercomparisons (Goldman; Paton-Walsh et al. 1999; Griffith; Jones et al. 2003; Meier; Paton-Walsh et al. 2005; Walsh; Bell et al. 1997) have yielded typical levels of agreement of 1-2% for tropospheric gases such as N<sub>2</sub>O and CO<sub>2</sub>, and agreement of 2-3% for stratospheric compounds such as HCl, HNO<sub>3</sub> and HF, with some instances of worse levels of agreement. The results of these earlier intercomparisons underlined the importance of a thorough knowledge of the spectrometer's instrumental line shape (ILS). More recently, better techniques have been developed to characterise the ILS using low-pressure gas cells, which have been adopted by all members of the infrared working group of the NDACC (Hase; Blumenstock et al. 1999) and were used to help characterise the two instruments' performance prior to starting the intercomparison. This intercomparison is the first to include a spectrometer built by the commercial company

“Bomem”. It is also unique in the sense that each different location presents different measurement challenges – the Arctic springtime provides an atmosphere that is rapidly varying with time and airmass.

## **2. Format of the Intercomparison**

The FTIR intercomparison described here was conducted at Environment Canada’s (EC) laboratory in Eureka, Nunavut during April and May in 1999. The facility is located at 80.05°N, 86.42°W, 610 metres above mean sea level. The Bomem DA8 interferometer permanently installed at Eureka was compared with the mobile BRUKER 120M operated by the National Physical Laboratory (NPL). Further details of the operation of these spectrometers can be found in the literature (Bell; PatonWalsh et al. 1996; Bell; Walsh et al. 1998; Kerzenmacher; Walker et al. 2005; Mahieu; Zander et al. 2005; Wiacek; Jones et al. 2006; Farahani; Fast et al. 2007). The two spectrometers were operated on the same floor within 2m of each other, using separate solar trackers. Spectra were recorded nearly simultaneously except that the EC instrument records only when the mirror scans away from the zero path difference position whilst the NPL instrument records in both directions of the moving mirror. So the time taken to record a single spectrum is similar for both spectrometers, but two spectra were recorded on the NPL instrument for each EC spectrum. Simultaneous measurement is of particular importance at such high latitudes as the species of interest are known to vary quite rapidly in short time scales (Bell; Walsh et al. 1998).

The intercomparison consisted of an “open” phase, when the performance of the instruments and the results of analysis of the spectra could be openly discussed, and a “blind” phase when no exchange of information was permitted between the two groups. The results of analysis of

spectra recorded in this blind phase were sent to an independent referee (A. Meier) for collation and comparison.

### 3. Preparation of the Spectrometers

Both spectrometers were equipped with an indium-antimonide (InSb) detector and a mercury cadmium telluride (MCT) detector. The NPL instrument used a potassium bromide (KBr) beamsplitter with the MCT detector and an optical filter with a band-pass from  $700\text{cm}^{-1}$  to  $1050\text{cm}^{-1}$ . A calcium fluoride ( $\text{CaF}_2$ ) beamsplitter was used with the NPL InSb detector along with three optical filters with a band-passes from  $2000\text{cm}^{-1}$  to  $2600\text{cm}^{-1}$ ;  $2400\text{cm}^{-1}$  to  $3200\text{cm}^{-1}$ ; and  $3950\text{cm}^{-1}$  to  $4400\text{cm}^{-1}$ . The EC instrument used a KBr beamsplitter for both detectors and the following band-pass filters:  $650\text{cm}^{-1}$  to  $1250\text{cm}^{-1}$ ;  $2400\text{cm}^{-1}$  to  $3100\text{cm}^{-1}$ ;  $2750\text{cm}^{-1}$  to  $3100\text{cm}^{-1}$  and  $3950\text{cm}^{-1}$  to  $4300\text{cm}^{-1}$ .

After the NPL mobile spectrometer had been re-assembled and installed alongside the EC spectrometer, the alignment of each instrument was tested using low-pressure gas cells. A glass cell with KBr windows containing a low pressure of either  $\text{N}_2\text{O}$  or HBr gas was placed in the beam of the spectrometer. The first cell used was 2cm in length, containing 2mbar of HBr. The second cell was 5cm in length with 0.8mbars of  $\text{N}_2\text{O}$ . Spectra were recorded with each instrument's InSb detector using the HBr cell with either an internal infra-red source or the sun. Other spectra were recorded on the MCT and InSb detectors using the  $\text{N}_2\text{O}$  cell and the internal infra-red source. All these spectra were analysed using LINEFIT (Hase; Blumenstock et al. 1999) to derive two parameters that describe the instrumental line-shape (ILS). The first parameter is the modulation efficiency at maximum optical path difference (250cm for the Bomem and 257 cm for the Bruker) and the second parameter is the phase error, a measure of the asymmetry of the ILS. For measurements on both instruments and both detectors the phase error

derived was small with a large standard deviation in the results from different lines and spectra used in the analyses. The modulation efficiency at maximum optical path difference was much more consistent with a mean and standard deviation of  $0.85 \pm 0.06$  for the EC Bomem DA8 spectrometer and  $0.87 \pm 0.04$  for the NPL Bruker 120M spectrometer. These results are typical of what can be achieved with these particular instruments and the participants were therefore satisfied that the spectrometers were well aligned, free from unusual problems and ready for the intercomparison to begin.

#### **4. Spectral Analysis**

Vertical column amounts were derived from each individual spectrum by iteratively adjusting the concentration of the target gas in a simulated spectral interval until the difference between the measured and simulated spectrum was minimised. The simulated spectrum was generated using spectral line parameters from the HITRAN 1996 compilation (Rothman; Rinsland et al. 1998) with solar lines simulated as described in (Rinsland; Jones et al. 1998). A layered model of the atmosphere was used, with the pressure, temperature and an initial concentration (or volume mixing ratio) for each gas assigned for every layer. The iterative fitting algorithm was constrained to allow only a scaling of the concentration profile for each gas (i.e. the concentration of the gas was multiplied by a single factor applied to all layers of the model). An ideal ILS (100% modulation at maximum optical path difference and zero phase error) was assumed for the two instruments in the analysis. Both groups used an identical algorithm to perform this non-linear iterative fitting, namely the SFIT spectral fitting code, version 1.09e.

A large effort was made to ensure that the ancillary data and spectral fitting parameters used by both groups were identical. The pressure and temperature (PT) data were taken from the radio sonde launched daily at 11 UT from the Eureka weather station. These were then splined with data from the National Center for Environmental Prediction (NCEP) assimilated for



Eureka's location and with a standard sub-arctic PT profile to produce a PT profile to be used by both groups. The initial concentration profiles for each day were generated by adjusting a standard set using a tropopause height estimated from the PT profile. The use of a single set of reference concentration profiles for all days (as had been done in earlier intercomparisons) was not practical because the air mass above Eureka in spring can be highly variable due to the effects of subsidence and the movement of the polar vortex relative to the site.

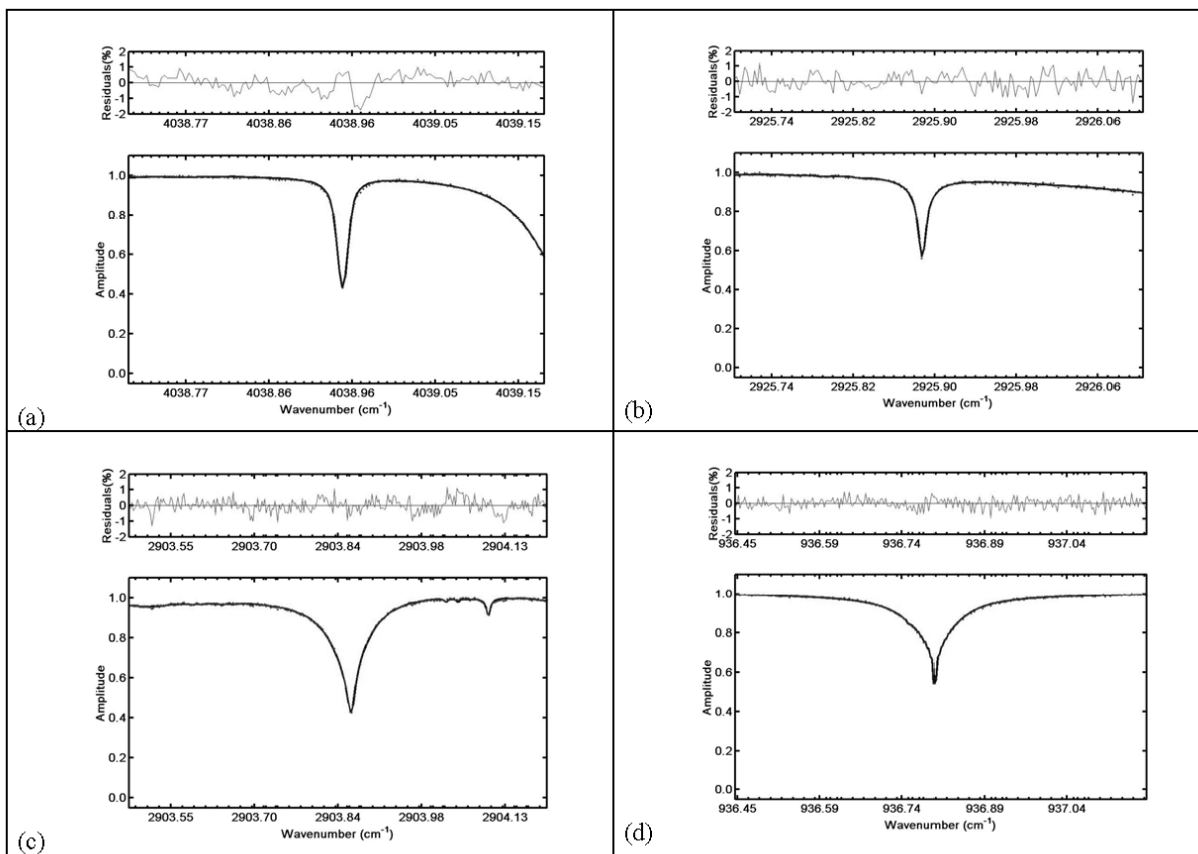
**Table 1:** The observation windows agreed upon for the analysis of key molecules. The last column lists interfering molecules that were taken into account in the analysis. Molecules that were actively fitted are indicated by an (F). Molecules which were pre-scaled to a total column amount retrieved in another, interference free, micro-window and held constant in the final retrieval for species are marked (C).

Principal Molecule	Fit Region (cm <sup>-1</sup> )	Other Gases Included	
		C-Const(fixed)	F-Fitted
HF	4038.70-4039.18	H <sub>2</sub> O (F), CH <sub>4</sub> (F), solar (F), HDO (C)	
HCl	2925.70-2926.10	CH <sub>4</sub> (C), H <sub>2</sub> O(C), NO <sub>2</sub> (F)	
O <sub>3</sub>	2775.78 -2775.88	HCl (F), N <sub>2</sub> O (F), CH <sub>4</sub> (F)	
CH <sub>4</sub>	2903.48-2904.20	H <sub>2</sub> O(F), HCl(F), HDO(F)	
CH <sub>4</sub>	2835.40-2835.87	HDO (F)	
N <sub>2</sub> O	2806.00-2806.80	CH <sub>4</sub> (F)	
N <sub>2</sub> O	2481.12-2482.50	CO <sub>2</sub> (F), CH <sub>4</sub> (F)	
N <sub>2</sub>	2418.40-2418.90	solar (F)	
HNO <sub>3</sub>	867.00-869.30	NH <sub>3</sub> (F)	
HNO <sub>3</sub>	872.25-874.80	H <sub>2</sub> O (F)	
CO <sub>2</sub>	2626.20-2627.06	HDO(C), CH <sub>4</sub> (C)	
CO <sub>2</sub>	936.44-937.18	--	

The exact frequency range or “micro-window” to be used for retrieving each gas and which interfering gases should be adjusted and which fixed were chosen to match those of earlier intercomparisons and varied only when local atmospheric conditions resulted in problems with the original micro-windows (such as saturation or excessive interference from water). The atmospheric continuum from water vapour, nitrogen and other gases is fitted as a single background parameter in all micro-windows. Details of the chosen micro-windows are given in Table 1.

## 5. Results

Once the referee had received all results from both groups, the derived vertical columns were released for both groups to see. The results were consistent with those seen in the open phase of the intercomparison: the level of agreement was generally a little worse than that seen in earlier intercomparison exercises (Goldman; Paton-Walsh et al. 1999; Griffith; Jones et al. 2003; Meier; Paton-Walsh et al. 2005; Walsh; Bell et al. 1997), with the most significant differences seen in HF. Whilst many of the differences lie within the one sigma standard deviation of the daily measurements from each instrument, there is a clear bias, with NPL columns consistently lower than EC columns for all gases derived from the InSb detectors. The picture is less clear for gases derived from the MCT but in these cases the NPL columns tend to be higher than EC columns. Fits to the data appeared good with no obvious differences in the quality of the fits between instruments. Examples of fits for HF, HCl, HNO<sub>3</sub> and CO<sub>2</sub> from spectra taken on the EC instrument are given in figures 1a – 1d.



**Figure 1:** Example of fits to spectral data taken on the EC Bomem DA8. The dotted line is the simulated fit to the measured data (solid line). Above each spectral interval the residual to the fit is shown (simulated – measured). Spectral windows illustrated are **(a)** Spectral window showing HF at  $4039\text{ cm}^{-1}$  **(b)** Spectral window showing HCl at  $2926\text{ cm}^{-1}$  **(c)** Spectral window showing CH<sub>4</sub> at  $2904\text{ cm}^{-1}$  and **(d)** Spectral window showing CO<sub>2</sub> at  $936\text{ cm}^{-1}$ .

For column amounts derived from spectra recorded on InSb detectors the mean percentage differences found over the three days from the two different spectrometers was 6.7% for HF (at  $4039\text{ cm}^{-1}$ ); 2.7% for HCl (at  $2926\text{ cm}^{-1}$ ); 3.8%; for CH<sub>4</sub> (at  $2904\text{ cm}^{-1}$ ); 2.9%; for CH<sub>4</sub> (at  $2835\text{ cm}^{-1}$ ); 2.4% for N<sub>2</sub>O (at  $2806\text{ cm}^{-1}$ ); 3.2% for N<sub>2</sub>O (at  $2482\text{ cm}^{-1}$ ); 3.2% for O<sub>3</sub> (at  $2776\text{ cm}^{-1}$ ); 3.8% for CO<sub>2</sub> (at  $2627\text{ cm}^{-1}$ ); and 2.8% for N<sub>2</sub> (at  $2419\text{ cm}^{-1}$ ) with the mean NPL column lower in all cases.

For column amounts derived from spectra recorded on MCT detectors the mean percentage differences found over the three days from the two different spectrometers was 1.2% for CO<sub>2</sub> (at

936  $\text{cm}^{-1}$ ); 2.6% for  $\text{HNO}_3$  (at 873  $\text{cm}^{-1}$ ) and 2.4% for  $\text{HNO}_3$  (at 868  $\text{cm}^{-1}$ ) with the mean NPL column generally higher than the mean EC column. The results are presented in full in Table 2.

## 6. Discussion of the Results

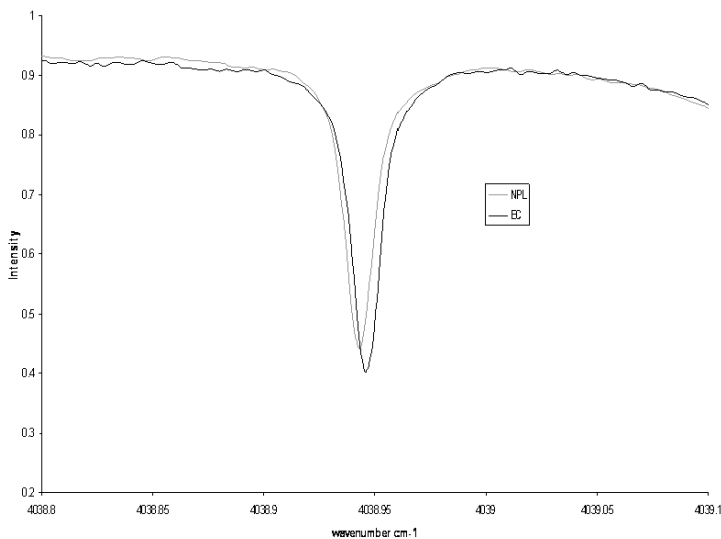
The level of agreement between the two instruments is around 3% for nearly all of the gases. The results are similar for broad tropospheric absorbers such as  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$  and narrow stratospheric absorbers such as  $\text{HCl}$  and  $\text{O}_3$ . The results are also similar for  $\text{HNO}_3$  and  $\text{CO}_2$  measured on the MCT detectors. The previous intercomparison results showed agreement between the NPL spectrometer and the spectrometer at Kiruna, Sweden of approximately 1% for all InSb species and 3% for MCT species (Meier; Paton-Walsh et al. 2005), with the MCT results improving to 1% after correction for detector non-linearity. Therefore these results are comparable for the MCT species  $\text{HNO}_3$  and  $\text{CO}_2$  but significantly worse for InSb species. In particular the derived HF column amounts are typically different by over 5%.

Large differences in HF have been seen before (Griffith; Jones et al. 2003); the magnitude and direction of this difference is similar to that observed between the NPL instrument and the instrument operated by the National Institute of Water and Atmospheric Research (NIWA) at Lauder, New Zealand. If we make the assumption that the performance of the NPL instrument is unaltered - despite having been dismantled, transported, reassembled and re-aligned in addition to having a new InSb detector - then we could infer that the spectrometers at Eureka and Lauder might agree whilst being ~ 5% different from the NPL and Kiruna spectrometers.

**Table 2:** For each micro-window analysed the mean vertical column amount of the trace gas derived from the spectra from each instrument is shown for each day, along with the percentage standard deviation of this vertical column amount. The percentage difference between the mean column amount derived from the NPL spectrometer and the mean column amount derived from the EC spectrometer is given in the last column. Finally the mean percentage difference for all three days is shown in bold to highlight biases in the results.

	<b>Date</b>	<b>NPL Column &amp; Std dev</b>	<b>EC Column &amp; Std dev</b>	<b>% Difference</b>
HF (4039 cm <sup>-1</sup> )	April 30 <sup>th</sup>	1.87E+15	2.2 % 1.98E+15	2.6 % -5.6
	May 1 <sup>st</sup>	2.09E+15	1.1 % 2.30E+15	1.6 % -9.1
	May 2 <sup>nd</sup>	2.06E+15	0.8 % 2.18E+15	2.7 % -5.5
<b>∴ Mean percentage difference for HF = - 6.7%</b>				
HCl (2926 cm <sup>-1</sup> )	April 30 <sup>th</sup>	6.11E+15	2.1 % 6.30E+15	3.2 % -3.0
	May 1 <sup>st</sup>	6.77E+15	1.0 % 7.06E+15	2.1 % -4.1
	May 2 <sup>nd</sup>	6.91E+15	0.9 % 6.97E+15	2.0 % -0.9
<b>∴ Mean percentage difference for HCl = - 2.7%</b>				
CH <sub>4</sub> (2904 cm <sup>-1</sup> )	April 30 <sup>th</sup>	3.34E+19	1.2 % 3.50E+19	3.2 % -4.5
	May 1 <sup>st</sup>	3.26E+19	0.5 % 3.39E+19	2.3 % -3.8
	May 2 <sup>nd</sup>	3.24E+19	0.5 % 3.34E+19	2.0 % -3.0
<b>∴ Mean percentage difference for CH<sub>4</sub> at (2904 cm<sup>-1</sup>) = - 3.8%</b>				
CH <sub>4</sub> (2835 cm <sup>-1</sup> )	April 30 <sup>th</sup>	3.43E+19	1.2 % 3.49E+19	2.3 % -1.7
	May 1 <sup>st</sup>	3.34E+19	1.5 % 3.54E+19	2.2 % -5.6
	May 2 <sup>nd</sup>	3.32E+19	1.0 % 3.37E+19	2.3 % -1.5
<b>∴ Mean percentage difference for CH<sub>4</sub> at (2835 cm<sup>-1</sup>) = - 2.9%</b>				
N <sub>2</sub> O (2806 cm <sup>-1</sup> )	April 30 <sup>th</sup>	5.98E+18	2.4 % 6.15E+18	3.3 % -2.8
	May 1 <sup>st</sup>	5.82E+18	2.1 % 5.99E+18	2.4 % -2.8
	May 2 <sup>nd</sup>	5.74E+18	1.3 % 5.83E+18	5.1 % -1.5
<b>∴ Mean percentage difference for N<sub>2</sub>O at (2806 cm<sup>-1</sup>) = - 2.4%</b>				
O <sub>3</sub> (2776 cm <sup>-1</sup> )	April 30 <sup>th</sup>	9.24E+18	4.4 % 9.59E+18	3.1 % -3.6
	May 1 <sup>st</sup>	9.58E+18	3.3 % 1.00E+19	2.0 % -4.6
	May 2 <sup>nd</sup>	9.21E+18	2.6 % 9.36E+18	1.7 % -1.6
<b>∴ Mean percentage difference for O<sub>3</sub> at (2776 cm<sup>-1</sup>) = - 3.2%</b>				
CO <sub>2</sub> (2626 cm <sup>-1</sup> )	April 30 <sup>th</sup>	7.65E+21	1.9 % 8.00E+21	4.8 % -4.4
	May 1 <sup>st</sup>	7.57E+21	0.8 % 7.83E+21	1.2 % -3.4
	May 2 <sup>nd</sup>	7.56E+21	1.3 % 7.82E+21	3.0 % -3.4
<b>∴ Mean percentage difference for CO<sub>2</sub> at (2626 cm<sup>-1</sup>) = - 3.8%</b>				
N <sub>2</sub> O (2482 cm <sup>-1</sup> )	April 30 <sup>th</sup>	5.89E+18	0.9 % 6.10E+18	2.0 % -3.4
	May 1 <sup>st</sup>	5.74E+18	0.4 % 6.02E+18	1.4 % -4.8
	May 2 <sup>nd</sup>	5.71E+18	0.3 % 5.80E+18	1.1 % -1.6
<b>∴ Mean percentage difference for N<sub>2</sub>O at (2482 cm<sup>-1</sup>) = - 3.2%</b>				
N <sub>2</sub> (2419 cm <sup>-1</sup> )	April 30 <sup>th</sup>	1.67E+25	3.8 % 1.70E+25	5.4 % -2.2
	May 1 <sup>st</sup>	1.65E+25	2.4 % 1.77E+25	4.1 % -7.2
	May 2 <sup>nd</sup>	1.64E+25	3.4 % 1.62E+25	2.4 % 0.8
<b>∴ Mean percentage difference for N<sub>2</sub> = -2.8%</b>				
CO <sub>2</sub> (936 cm <sup>-1</sup> )	April 30 <sup>th</sup>	7.49E+21	0.9 % 7.13E+21	0.6 % 5.0
	May 1 <sup>st</sup>	7.20E+21	0.5 % 7.19E+21	0.7 % 0.0
	May 2 <sup>nd</sup>	7.28E+21	0.5 % 7.38E+21	0.9 % -1.4
<b>∴ Mean percentage difference for CO<sub>2</sub> at (936 cm<sup>-1</sup>) = + 1.2%</b>				
HNO <sub>3</sub> (873 cm <sup>-1</sup> )	April 30 <sup>th</sup>	1.81E+16	1.8 % 1.67E+16	2.0 % 8.6
	May 1 <sup>st</sup>	2.01E+16	0.8 % 2.01E+16	1.2 % 0.0
	May 2 <sup>nd</sup>	1.97E+16	3.0 % 1.98E+16	0.8 % -0.8
<b>∴ Mean percentage difference for HNO<sub>3</sub> at (873 cm<sup>-1</sup>) = +2.6%</b>				
HNO <sub>3</sub> (868 cm <sup>-1</sup> )	April 30 <sup>th</sup>	2.00E+16	2.8 % 1.94E+16	2.1 % 3.0
	May 1 <sup>st</sup>	2.30E+16	0.8 % 2.22E+16	0.9 % 3.6
	May 2 <sup>nd</sup>	2.20E+16	1.3 % 2.18E+16	1.1 % 0.8
<b>∴ Mean percentage difference for HNO<sub>3</sub> at (868 cm<sup>-1</sup>) = +2.4%</b>				

In the analyses described above an ideal ILS was assumed for both instruments. This was done so that the intercomparison would be directly comparable to other recent NDACC intercomparisons (Goldman; Paton-Walsh et al. 1999; Griffith; Jones et al. 2003; Meier; Paton-Walsh et al. 2005). A sensitivity test was performed by reanalysing the NPL spectra for HF column amounts with the true ILS as measured by the LINEFIT software included in the forward model. The results were compared to the analysis that assumed an ideal ILS and it was found that the derived vertical column values changed by less than 1%. The estimates of the true ILS were very similar for the two instruments and so it was concluded that instrument line shape problems were not likely to be the main cause of the differences in columns derived from the two instruments. It should be noted that the HBr absorption features used to derive the ILS are around  $2400\text{cm}^{-1}$  and that the ILS is known to vary with wavenumber {Griffith, 2003 #35}, so the measured ILS may not accurately reflect the true ILS at the HF absorption around  $4038\text{cm}^{-1}$ .



**Figure 2:** Shown in black is the HF line from the first spectrum recorded on the EC spectrometer on May 1<sup>st</sup> 1999. Overlaid in grey is the spectrum recorded simultaneously on the NPL instrument. Both spectra have been normalised by dividing by the peak intensity value.

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Figure 2 shows an example pair of HF lines from simultaneous spectra. Differences can be seen in both the x-axis (frequency in wavenumbers) and y-axis (arbitrary intensity). The spectral calibration (or frequency calibration) of the x-axis is done by reference to a temperature stabilized visible helium-neon laser that is input through the same optical path as the infrared source, is modulated by the interferometer and measured at the detector . The sampling of the interferogram is done at every zero crossing of the laser and the frequency of the laser is input into the instruments' software to calibrate the frequency scale. Phase errors can cause a shift in frequency but the two instruments' will also have a different frequency scale if the lasers stabilize at slightly different temperatures or if a different frequency value is entered into the software of each instrument. Since the analysis algorithm performs a multiplicative frequency shift to line up known absorptions with the lines in the HITRAN database this will not produce any significant difference between the column amounts derived from each instrument.

The y-axis of each spectrum is intensity in arbitrary units. It depends upon the intensity envelope of the interferogram (the intensity of radiation reaching the detector at each frequency). The intensity envelope is determined as the moving mirror of the interferometer passes through the point where the fixed and moving mirrors are at an equal distance from the beam-splitter. This point is called zero path difference (ZPD) and is the point at which all frequencies of radiation will constructively interfere. The shape of the intensity envelope will depend upon the black-body emission from the sun, the optical characteristics of components of the spectrometer (eg beamsplitter, mirrors and optical filters) and the sensitivity of the detector to different frequencies of radiation.

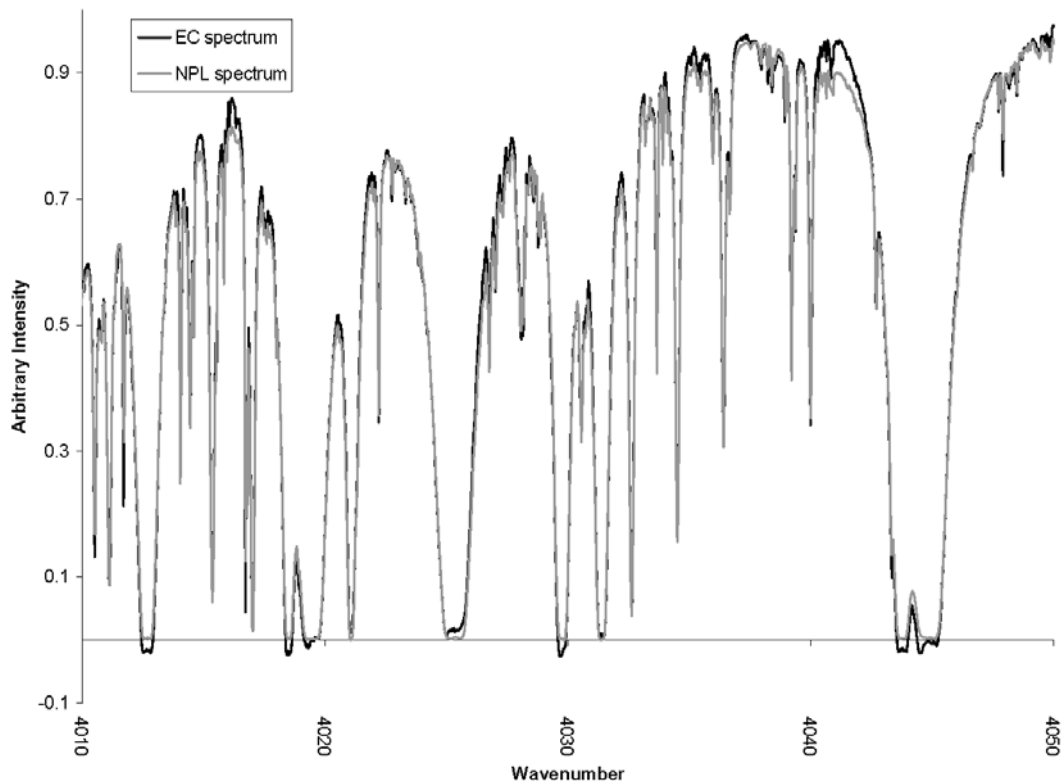
Absorption features from atmospheric gases reduce the intensity from the intensity envelope (the 100% level) at certain characteristic frequencies. The analysis of spectra involves determining the area of absorption features below this 100% level intensity. Since absorption

features are measured with respect to the 100% level the actual gain applied to the signal intensity coming from the detector is not important. What is of fundamental importance is the definition of the intensity envelope as the moving mirror passes through ZPD. If this is distorted then the whole spectrum may be shifted (in a way that can vary with frequency) producing errors in the zero and 100% levels.

## **7. Comparison of zero and 100% levels**

Seven pairs of simultaneous spectra from each instrument were normalised and then the 100% levels near the HF line and the peak transmission levels of the HF line were compared. The one hundred percent levels were similar in the two instruments' spectra but the HF line was consistently and significantly deeper in the EC spectra (peak transmission of  $0.466 \pm 0.010$ ) than in the NPL spectra (peak transmission of  $0.494 \pm 0.003$ ). Taking the natural logarithms of the peak transmissions ( $[\ln(0.494)]/[\ln(0.466)] = 0.926$ ) the expected difference in derived columns could be very approximately estimated to be -7.4%. This calculation neglects the fact that the field of view of the two instruments is different (3mrads for NPL and 1.7mrads for EC), which would reduce the estimated discrepancy between the two instruments. (Using a larger field of view broadens the ILS and thus broadens the HF line and decreases its depth.) This inspection confirmed that there are differences in the spectra recorded by the two instruments which are causing the differences in derived columns, rather than errors in the analysis procedure. The differences in peak transmission could be due to an error in the correct definition of the intensity envelope of the interferogram causing errors in the zero level (or 100% level) in either or both of the spectrometers.

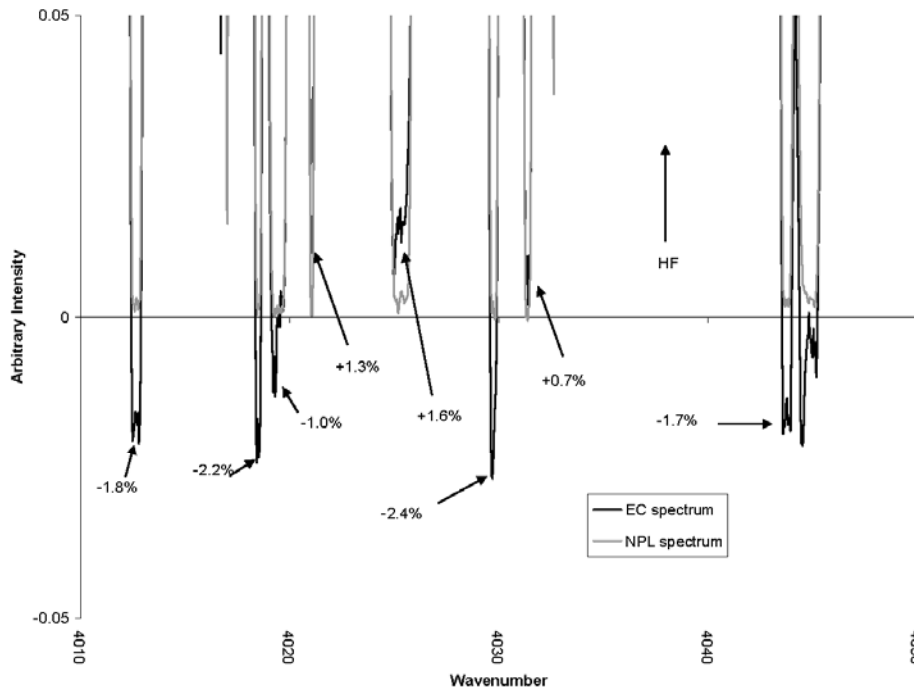




**Figure 3:** Shown in black is a detail of the first spectrum recorded on the EC spectrometer on May 1<sup>st</sup> 1999 in the region used to derive HF column amounts. Overlaid in grey is the spectrum recorded simultaneously on the NPL instrument. Both spectra have been normalised by dividing by the peak intensity value. Differences in the definition of the zero level can clearly be seen.

The first spectrum recorded on the EC spectrometer on May 1<sup>st</sup> 1999 in the region used to derive HF column amounts is shown in Figure 3 alongside the spectrum recorded simultaneous on the NPL instrument. Both spectra have been normalised by dividing by the peak intensity value. Differences in the position of the zero level can clearly be seen. These two spectra were chosen as examples because the magnitudes of the zero-offsets are typical for spectra from each instrument. Figure 4 shows the same spectra expanded so that the zero level offsets can be seen more clearly. For better clarity only the EC zero levels for saturated features are marked. The EC spectrum displays significant variation in the zero level for different saturating features with

values as low as -2.4% and as high as +1.6%. A possible physical cause of this is clipping of the interferogram after zero path difference – possibly at the gain switching point. The NPL spectrum is more consistent but the zero level is also not perfect with values varying from zero to +0.2%.



**Figure 4:** Shows the same spectra as Figure 3 expanded to show the zero level offsets more clearly. The EC spectrum is shown in black and the zero levels are given for all saturated features. The NPL spectrum is shown in grey for comparison.

The zero-offsets for individual saturating features are not always consistent from one spectrum to the next. Regions of the spectrum that show positive offsets in some spectra may show negative offsets in others. Taking two saturating features (one either side of the HF feature) to illustrate the problem: the average zero-offset between 4031.3 and 4088.45  $\text{cm}^{-1}$  is  $-0.68 \pm 1.4 \%$  for the EC instrument and  $0.09 \pm 0.23 \%$  for the NPL instrument, whilst the average zero-offset between 4088.0 and 4088.3  $\text{cm}^{-1}$  is  $-2.6 \pm 1.3 \%$  for the EC instrument and  $0.23 \pm 0.18 \%$  for the

NPL instrument. The relatively small zero-offsets seen in the NPL spectra may be explained by the non ideal ILS, but the larger offsets in the EC spectra seem too large to be explained by the phase error alone. The example spectra shown in figure 3 have similar 100% levels from 4030  $\text{cm}^{-1}$  to 4038  $\text{cm}^{-1}$ , but they diverge from 4038  $\text{cm}^{-1}$  to 4041  $\text{cm}^{-1}$ . This might possibly be caused by differences in the transmission and reflection properties of the optical components of the two instruments but is more likely to be the result of distortion of the intensity envelope of the interferogram, suggesting that some problem with the signal generation at ZPD is causing the zero level offsets and ultimately resulting in a bias in the retrieved column amounts.

The spectral analysis code, SFIT 1.09e, allows the zero level to be fixed at an appropriate level for a given region of the spectrum. The difficulty in this case is determining what zero level should be assumed because of the large variations between adjacent saturated features. A sensitivity study was performed by reanalysing the EC spectra for HF column amounts with the zero level set to different values. It was found that a negative offset in the zero level resulted in a derived HF column that was lower by a factor approximately 1.4 times the magnitude of the offset. For example, an assumed offset of -3% produced an HF column that was  $3 \times 1.4 = 4.2\%$  lower than the HF column derived when the zero level was fixed at zero. From this we may conclude that the problems with the zero levels may account for a significant portion of the differences between the spectrometers but on their own may not explain all of the differences. We recommend that when analysing spectra from the EC spectrometer the zero-level is fixed at an appropriate level for the region of interest in each individual spectrum.

As a result of this work we have re-inspected the spectra recorded during the intercomparison at Lauder in the region used to derive HF. We found that the spectra recorded on the NIWA instrument also had imperfect definition of the zero level with negative offsets of about 2% at the

saturated feature around  $4045\text{ cm}^{-1}$ . This provides a possible explanation for a large portion of the differences observed during that earlier intercomparison. The NIWA instrument underwent a major re-alignment after the intercomparison and the spectra recorded after this had well defined zero levels.

## 8. Conclusions

An intercomparison of two ground-based Fourier transform infrared spectrometers at Eureka, Canada revealed typical differences of around 3% for most trace gases and differences in excess of 5% for HF. These differences are much larger than the preceding NDACC intercomparison at Kiruna but not significantly larger than another earlier NDACC intercomparison (Griffith; Jones et al. 2003; Walsh; Bell et al. 1997). A likely cause for a substantial portion of the differences observed is the poor definition of the zero level in the spectra from the EC instrument. A possible physical cause of this is clipping of the interferogram after zero path difference – possibly at the gain switching point. The zero level offsets may be input into the retrieval code to make a partial correction for this effect, thereby improving the level of agreement between the instruments. Further reductions in the differences can be expected when the measured instrument line-shape is included in the model for the simulated spectrum used in the fitting algorithm. We conclude that instrumental differences contribute to the uncertainties in derived column amounts of trace gases in the atmosphere. Despite the larger differences seen in this intercomparison, these instrumental differences are comparable or smaller than the combined effects of the uncertainties in the assumed pressure and temperature profiles, the choice of spectral fitting region and the treatment of interfering gases.

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## Figure Captions

**Figure 1:** Example of fits to spectral data taken on the EC Bomem DA8. The dotted line is the simulated fit to the measured data (solid line). Above each spectral interval the residual to the fit is shown (simulated – measured). Spectral windows illustrated are **(a)** Spectral window showing HF at  $4039\text{ cm}^{-1}$  **(b)** Spectral window showing HCl at  $2926\text{ cm}^{-1}$  **(c)** Spectral window showing CH<sub>4</sub> at  $2904\text{ cm}^{-1}$  and **(d)** Spectral window showing CO<sub>2</sub> at  $936\text{ cm}^{-1}$

**Figure 2:** Shown in black is the HF line from the first spectrum recorded on the EC spectrometer on May 1<sup>st</sup> 1999. Overlaid in grey is the spectrum recorded simultaneously on the NPL instrument. Both spectra have been normalised by dividing by the peak intensity value.

**Figure 3:** Shown in black is a detail of the first spectrum recorded on the EC spectrometer on May 1<sup>st</sup> 1999 in the region used to derive HF column amounts. Overlaid in grey is the spectrum recorded simultaneously on the NPL instrument. Both spectra have been normalised by dividing by the peak intensity value. Differences in the definition of the zero level can clearly be seen.

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