Inter-calibration of medium-resolution grating spectrometers for MOPITT validation

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ABSTRACT

The validation of MOPITT measurements of atmospheric carbon monoxide (CO) and methane (CH_4) will require independent, simultaneous, co-located measurements from ground- and aeroplane-based instruments. Recently, a program of MOPITT validation measurements in Russia and Canada has been proposed. This program will use three (nearly) identical Russian-made medium-resolution grating spectrometers (known as Sarcophagus) capable of measuring the atmospheric column concentration of CO and CH_4. Two of these instruments are located in Russia, and one in Canada. The similarity of these instruments provides the opportunity of acquiring a highly correlated validation dataset from diverse locations around the globe. As part of this program, we are proposing to inter-calibrate these instruments using a set of standard gas cells. These cells will be regularly shipped between the instruments for calibration and inter-comparison purposes. These measurements will be made relative to measurements from a very high-resolution Difference Frequency Laser Spectrometer (DFLS) located at the University of Toronto. In this paper we present the results of a test of this inter-calibration experiment using a single CO gas cell and involving a Sarcophagus, a high resolution Fourier Transform Spectrometer (FTS) and the University of Toronto DFLS.

Keywords: inter-calibration, inter-comparison, validation, remote sounding, spectrometry, retrieval, MOPITT

1. INTRODUCTION

Carbon monoxide (CO) and Methane (CH_4) are two atmospheric species which play an important role in the chemistry of the lower atmosphere of the Earth. The MOPITT satellite instrument, which will be launched this year on NASA's EOS Terra satellite, will globally measure these atmospheric species from a polar orbit around the Earth (*Drummond et al., 1993*). MOPITT is a nadir, or surface viewing instrument which utilises four length modulated radiometers (LMR) and two pressure modulator radiometers (PMR) tuned to 2130 cm^{-1} (4.7 µm) and 4260 cm^{-1} (2.35 µm) bands of CO, and the 2.3 µm band of CH_4 (*Tolton and Drummond 1997*, and *Taylor 1983*). An essential component of the MOPITT project will be the independent verification, or validation, of measurements from the MOPITT instrument. Validation is a fundamental component of any remote sensing satellite project, and involves the inter-comparison of measurements by a satellite sensor with other Earth-based measurements. It provides insight not only into the accuracy but also the believability of the satellite measurements, and can provide a means of developing and testing data retrieval algorithms.

The validation of MOPITT measurements of atmospheric CO and CH_4 will require independent simultaneous co-located measurements from ground- and aeroplane-based instruments. Since MOPITT is nadir viewing, a further requirement is that validation measurements be made over diverse locations and surface types around the world. As such, efforts have been made to enlist the help of numerous research scientists from around the world. One such effort

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has been a proposal to use a number of (nearly) identical Russian-made medium-resolution infrared grating spectrometers, known as Sarcophagus (*Dianov-Klokov, 1984*). These spectrometers, which are in operation in Canada, Russia, China and potentially Argentina, have been in use since the 1970's and are capable of measuring column amounts of atmospheric CO and CH_4 (*Dianov-Klokov et al., 1989*, and *Yurganov et al., 1999*).

One key component of the MOPITT global validation effort will be the inter-calibration of the various instruments that will make these measurements. A program of inter-calibration will have a number of problems to overcome. Two of the most difficult being the facts that the validation instruments will be located around the world and that the instruments will be of many types using different techniques. Recently, a global validation campaign was performed for the MAPS (Measurements of Pollution from Satellites) instrument. As part of this campaign, an international inter-calibration program was undertaken for the GC (Gas Chromatography) and GFCR (Gas Filter Correlation Radiometers) instruments taking part in the validation campaign (*Novelli et al., 1998*).

This paper describes a test of a proposed program of inter-calibration for MOPITT validation measurements made by three sarcophagus grating spectrometers in Russia (Zvenigorod, near Moscow, and Kislovodsk, in the Caucasus Mountains) and Canada (Toronto). The similarity of these instruments provides the opportunity of acquiring a highly correlated MOPITT validation dataset from diverse locations around the globe. It is also hoped that with the success of this program of inter-calibration, it might be expanded to include other instruments from other groups and/or institutions.

2. A PROPOSED INTER-CALIBRATION

We have proposed to calibrate and inter-compare the MOPITT validation measurements of three Sarcophagus spectrometers located in Canada and Russia, using a series of sealed gas cells. These cells, which would be shipped periodically to each spectrometer, would be used to calibrate the wavenumber scale and the instrument function for each instrument, and to inter-compare retrievals of gas amount. This inter-comparison would be made relative to measurements on the same gas cells by a very high resolution Difference Frequency Laser Spectrometer (DFLS) located at the University of Toronto. It is also hoped that this proposal for inter-calibration could be extended further to include other spectroscopic instruments such as Fourier Transform Spectrometers (FTS) and Gas Filter Correlation Radiometers (GFCR).

As a test of this inter-comparison proposal, we have performed an inter-comparison of retrievals on a single CO gas cell by three spectrometers: a medium-resolution Sarcophagus spectrometer, a high-resolution Bomem DA-8 FTS, and the University of Toronto DFLS.

2.1. The Gas Cell

Since it is impossible to fully simulate the variation in the physical properties of the atmosphere (such as pressure) in a gas cell, some thought was put into devising a gas cell which best approximates the atmosphere. To begin, the gas cell should contain an amount (molecules per cm^2) of CO similar to what would be observed in the real atmospheric column, which itself, varies with solar zenith angle (ϕ). The total number of molecules (N) per cm^2 in a vertical column is given by:

$$\frac{N}{cm^2} = 10^{-4}\frac{PN_a}{Mg\cos\phi}$$

where N_a is Avogadro's number, and M is the molecular mass of air. For a sea-level pressure P of 101.325 kPa, this corresponds to 2.147×10^{25} molecules cm^{-2} in the vertical column. For a typical Northern hemisphere CO mixing ratio of approximately 100 ppbv, this corresponds to 2.147×10^{18} CO molecules cm^{-2} in the vertical column. Also, since the

Table 1: Fill parameters of the gas cell.

Cell Length	Pressure	Temperature	Gas Mixture	CO Density
51.63 mm	50.25 kPa	21.3° C	5.06% CO, 94.94% N_2	3.23×10^{18} molec cm^{-2}

Table 2: Atmospheric CO mixing ratios as a function of solar zenith angle corresponding to the gas density in the CO gas cell.

CO Density	Corresponding CO Mixing Ratio as a Function of Solar Zenith Angle				
	$0°$ 2.15×10^{25}	$30°$ 2.48×10^{25}	$45°$ 3.04×10^{25}	$60°$ 4.3×10^{25}	$70°$ 6.3×10^{25}
3.23×10^{18} molec cm^{-2}	150 ppbv	130 ppbv	106 ppbv	75 ppbv	51 ppbv

mass-weighted average pressure of the atmosphere is approximately 50 kPa, the cells should have roughly the same pressure (P). The size of the cell was determined mostly from engineering consideration and was specified to be 38.1 mm wide and approximately 50 mm long (d). Given this design, the molecular number density in the cell will be given by:

$$\frac{N}{cm^2} = 10^{-4} \frac{P N_a d}{R T}$$

Given a temperature T of 20 °C, the molecular number density of the cell will be 6.18×10^{19} molecules cm^{-2}. For a CO mixing ratio of 5% (in Nitrogen), the CO number density of the cell would be 3.09×10^{18} molecules cm^{-2}, which corresponds to an atmospheric CO mixing ratio of approximately 144 ppbv in the vertical column. The physical parameters of the gas cell at the time of filling is shown in Table 1. For these parameters, the corresponding atmospheric CO mixing ratio as a function of solar zenith angle is shown in Table 2. A plot showing the calculated transmission of the cell in the 2130 cm^{-1} band of CO is shown in Figure 1.

For long-term stability, the cell was built out of glass, with $0.5°$ wedged CaF$_2$ windows (CaF$_2$ transmits infrared radiation and wedged to minimise fringing). The cell body was acid washed before the windows were glued on. The cell was then vacuum baked for two days before being filled. The cell was filled from a standard 5.06% CO in N$_2$ gas mixture. The cell was then sealed by gas flame. The walls of the cell were then insulated by a role of foam insulation and the temperature of the cell is measured using a high precision thermistor on the outer wall of the cell (underneath the insulation).
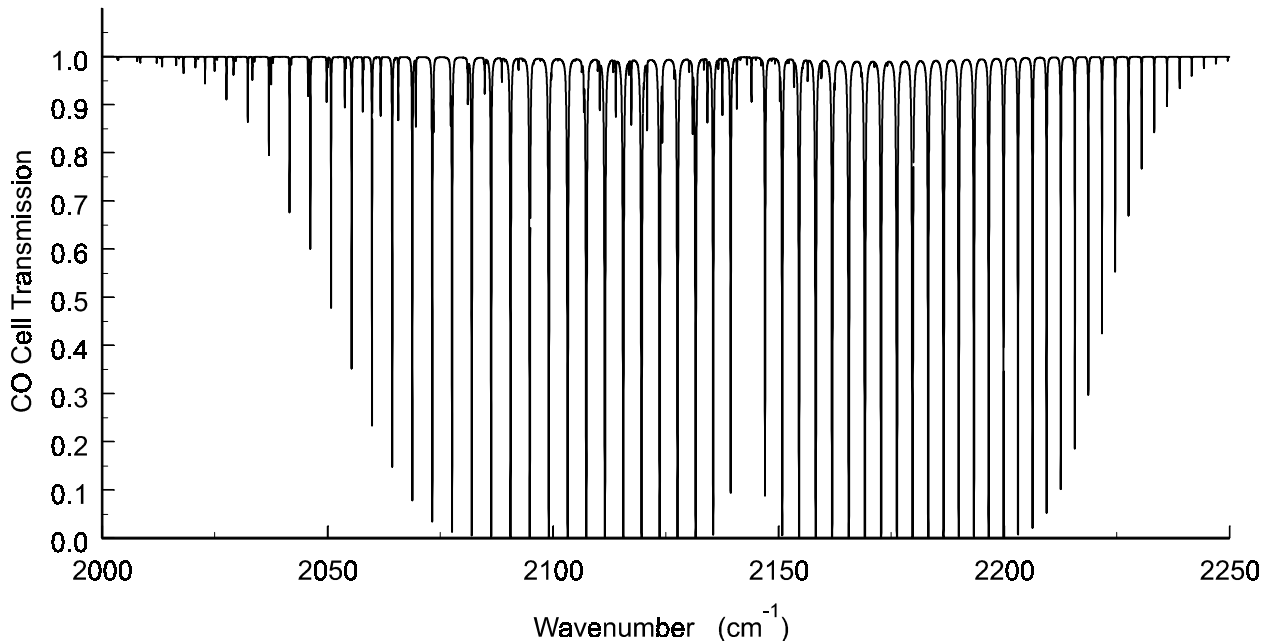

Figure 1: Transmission of the gas cell in the 2130 cm^{-1} band of CO.

3. INTER-CALIBRATION MEASUREMENTS

Spectral measurements of the transmission of the gas cell was made by three different instruments, a very high resolution DFLS, a high-resolution FTS, and a medium-resolution Sarcophagus. Retrievals of the gas pressure, and therefore gas density in the cell were performed using standard techniques for each instrument. For the Sarcophagus instrument, the retrieval techniques was the same as used for atmospheric measurements.

3.1. The University of Toronto Difference Frequency Laser Spectrometer

Measurements of the gas cell were performed using a DFLS located at the University of Toronto. This instrument has primarily been used to explore spectral line shapes in the infrared (*Sinclair et. al, 1997*, *Berman et al. 1997*, and *Duggan et al. 1993*). The DFLS creates a beam of infrared radiation tunable in the 2.5 to 5.5 μm by mixing the light from a frequency-stabilized Argon ion laser with the light from a Coherent 699-29, R6G dye laser. The two visible laser beams are overlapped and mixed in a nonlinear $LiIO_3$ crystal. In operation infrared power is normalized by splitting the infrared beam and monitoring the input and output signals from the following absorption cell with two identical liquid nitrogen cooled, InSb detectors. The maximum variation of the baseline signal was one part in 500 for a 1 cm^{-1} scan. The frequency measurement subsystem has as principal component a temperature stabilized, scanning Fabry-Perot interferometer used to determine the frequencies of both the dye and Argon ion laser relative to the frequency of a stabilized HeNe laser. Using this experimental setup, the resolution was of about 2 MHz (6×10^{-5} cm^{-1}) and the signal
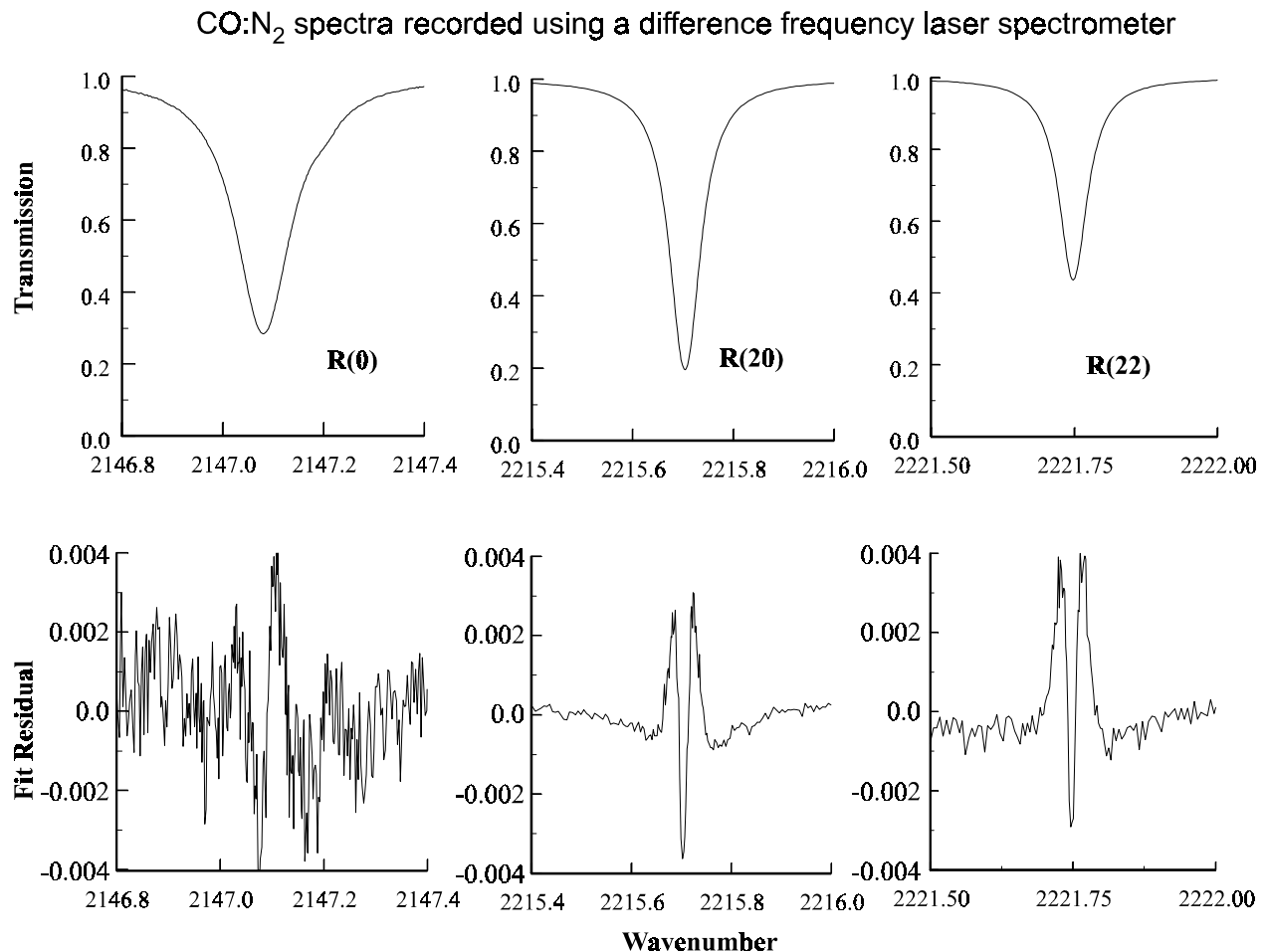

Figure 2: Retrieval of the CO amount in the cell using a DFS. Shown are the measured transmissions and fit residuals for the R(0), R(20), and R(22) lines of the 2130 cm^{-1} band of CO.

Table 3: Retrievals of molecular density of the gas cell using a high-resolution difference frequency spectrometer.

Spectral Line	Temperature (K)	Pressure (kPa)	Density (molec cm^{-2})	RMS Fit
R(0)	293.94	50.9025	3.263×10^{18}	0.188%
R(1)	293.89	50.7478	3.268×10^{18}	- -
R(2)	293.86	50.9798	3.283×10^{18}	- -
R(3)	293.82	50.9091	3.279×10^{18}	- -
R(19)	293.99	50.7692	3.268×10^{18}	- -
R(20)	293.99	50.7692	3.268×10^{18}	0.180%
R(22)	293.99	50.9291	3.278×10^{18}	0.133%
Average	**293.93**	**50.8581**	**3.272×10^{18}**	**0.167%**

to noise was close to 1500:1 for a 1 second integration time.

The spectral profile of each R branch line recorded with the DFLS have been fitted to a Voigt profile and an associated dispersion profile. The fitting program is described in *Berman (1998)*. Figure 2 shows measurements and fits of the R(0), R(20), and R(22) absorption lines of the gas cell. Table 3 details the retrievals of the cell pressure, temperature and density for measurements of seven lines in the R-branch. The measured average density of the cell as measured by the DFLS was 3.272×10^{18} molecules per cm^2.
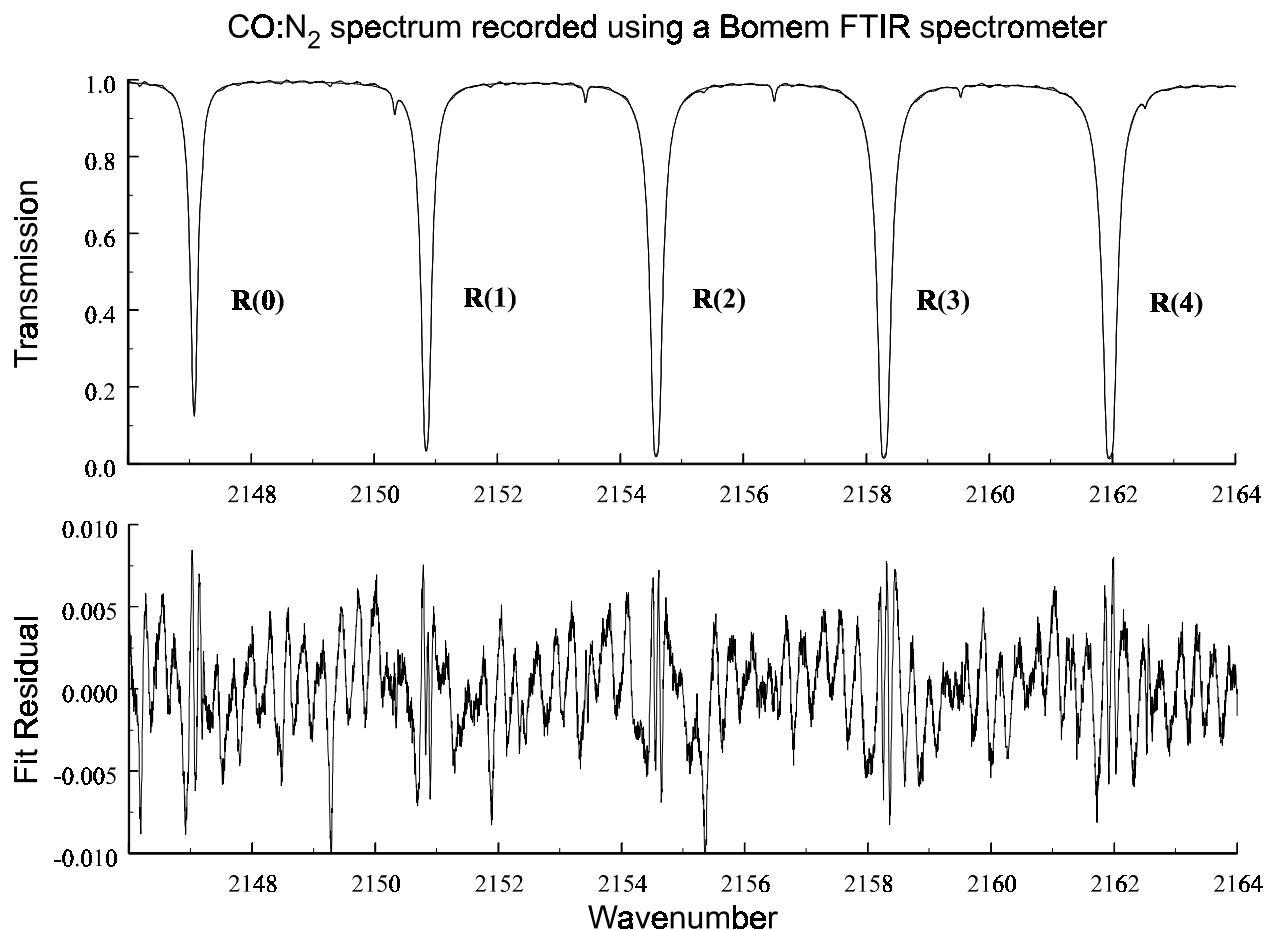

Figure 3: Retrieval of the CO amount in the cell using a Bomem DA-8 FTS. Shown are the measured transmissions and fit residuals for the R(0) through R(4) lines of the 2130 cm^{-1} band of CO.

Table 4: Retrievals of molecular density of the gas cell using a BOMEM DA-8 Fourier Transform Spectrometer (FTS).

Spectral Lines	Temperature (K)	Pressure (kPa)	Density (molec cm^{-2})	RMS Fit
R0, R1, R2, R3, R4 R19, R20, R22	293.99	50.909	3.277 × 10^{18}	0.281%

3.2. The Fourier Transform Spectrometer

The Fourier transform spectrum of the gas cell was recorded in the 2000-2250 cm^{-1} range and resolution of 0.008 cm^{-1} in ten consecutive runs using a commercial Bomem DA-8 FTS. An aperture of 5 mm was used and 200 scans were co-added to achieve a better signal to noise ratio. The spectral profiles recorded with the FTIR spectrometer were analysed using the multi-spectrum fit program developed by *Benner et al. (1995)*. The absorption were assumed to have Voigt line shapes. Initial values for the line positions and intensities were taken from the HITRAN96 database (*Rothman et al., 1998*). The foreign broadening parameters were fixed to the values reported in *Predoi-Cross et al. (1999)*, which are believed to be very high accuracy. The mixing ratio and pressure values were determined using successive fits of spectral segments of 25 cm^{-1}. The final values were chosen when the size of the residual was visibly reduced. Retrievals from the FTS spectra showed a gas cell density of 3.277 × 10^{18} molecules per cm^2, and are shown in Figure 3 and Table 4.

3.3. The Sarcophagus

Sarcophagus is a Russian-made Ebert/Fastie grating spectrometer with a 855 mm focal length and a 300 grooves mm^{-1} reflection grating. It was designed and constructed at the Institute of Atmospheric Physics of
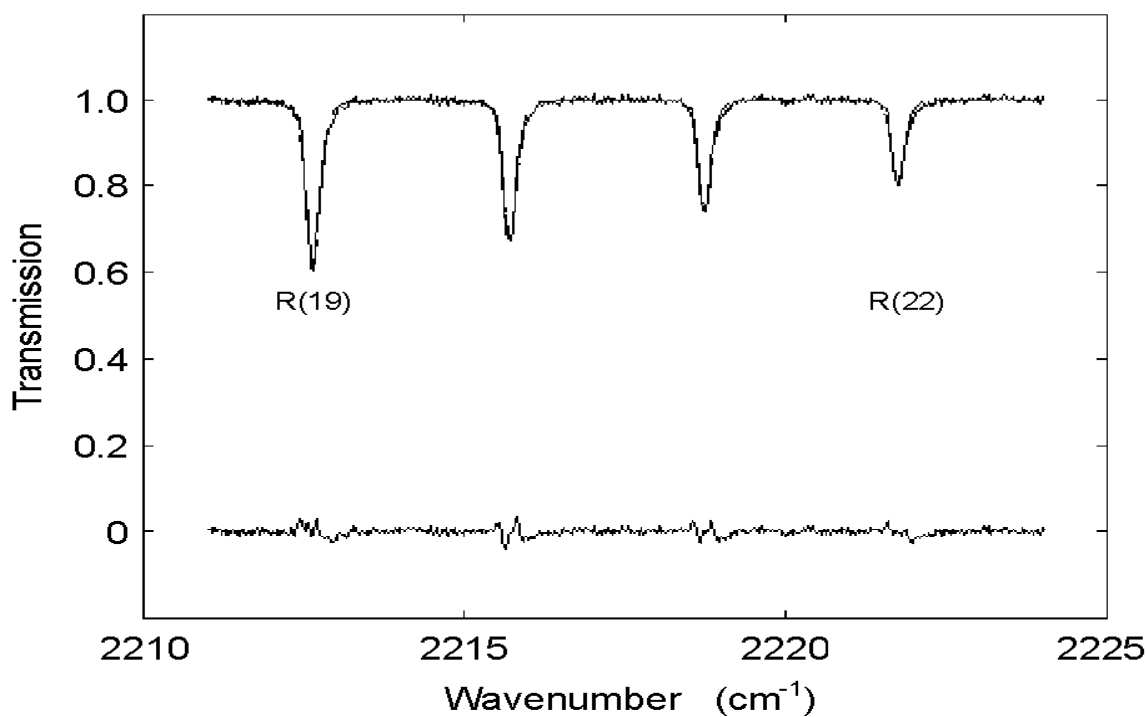

Figure 4: Retrieval of the CO amount in the cell using the sarcophagus. Shown are the measured transmissions and fit residuals for the R(19) through R(22) lines of the 2130 cm^{-1} band of CO.

Table 5: Retrievals of molecular density of the gas cell using the Sarcophagus.

Spectral Lines	Density (molec cm^{-2})	RMS Fit
R(19), R(20), R(21) & R(22)	3.295×10^{18}	0.83%

the Russian Academy of Science (*Dianov-Klokov, 1984*). In operation it provides a resolution nearly 0.2 cm^{-1} in the 2160 cm^{-1} spectral region. It has a Peltier cooled PbSe detector and a PC-based scan and data acquisition system.

Measurements of the transmission of the gas cell were made and a sample measurement is shown in Figure 4. Retrieval of the gas density was performed using a least squares minimisation technique recently developed for atmospheric retrievals with Sarcophagus (*McKernan et al., 1999*). The retrieved gas density was 3.295×10^{18} molecules per cm^2, and is shown in Table 5.

4. SUMMARY

We have preformed a test of a proposed inter-calibration three Russian-made "Sarcophagus" grating spectrometers located in Canada and Russia. This inter-calibration is to involve a series of gas cells which will be shipped between spectrometers and used for calibration and inter-comparison of retrievals. These measurements will be made relative to measurements from a very high-resolution Difference Frequency Laser Spectrometer (DFLS) located at the University of Toronto. This test involved an inter-calibration experiment using a single CO gas cell and involving a Sarcophagus, a high resolution Fourier Transform Spectrometer (FTS) and the University of Toronto DFLS. The gas cell was made out of glass with wedged CaF$_2$ windows, and was sealed by gas flame. Spectral measurements of absorption lines in the 2130 cm^{-1} band of CO and gas density retrievals were performed using all three spectrometers. The results are summarised in Table 6. Using the retrievals of the DFLS as a benchmark, the retrievals of the FTS and the Sarcophagus were 0.15% and 0.7% higher, respectively. The directly measured CO density at the time of filling the cell was 1.3% below the DFLS measurement. This was probably due to the sealing of cell as localised heating of the fill tube might have slightly increased the total CO density of cell.

The next step in this program of inter-calibration will be the shipping of the gas cell to Russia, for inter-comparison with the two Russian Sarcophagi spectrometers. Also, further measurements of the gas cell by the DFLS will be performed to see if the CO in the cell has remained stable over time. These steps will begin in the fall of 1999. It is also hoped that other groups involved in MOPITT validation will be interested in joining this experiment.

ACKNOWLEDGEMENTS

Table 6: A comparison of the measured CO gas density inside the gas cell at time of fill and the retrievals by the three spectrometers.

	Instrument Function Width (cm^{-1})	Retrieved CO Density (Molecules cm^{-2})	RMS Fit	Difference from DFLS Measurement
Fill	- -	3.23×10^{18}	- -	-1.3 %
DFLS	6×10^{-5}	3.272×10^{18}	0.167%	0 %
Bomem FTS	0.008	3.277×10^{18}	0.281%	0.15 %
Sarcophagus	0.2	3.295×10^{18}	0.83%	0.7 %

REFERENCES

Benner, C. D., C. P. Rinsland, V. M. Devi, M. A. H. Smith, and D. Atkins, "A Multispectrum Nonlinear Least Squares Fitting Technique," *J. Quant. Spectrosc. Radiat. Transfer*, **53**, 705 (1995).

Berman R., P. Duggan, P.M. Sinclair, A. D. May, and J.R. Drummond, *J. Mol. Spectrosc.* **181**, 350-363 (1997).

Berman, R., *Ph.D. Thesis*, University of Toronto, 1998.

Connors, V. S., B. B. Gormsen, S. Nolf, and H. G. Reichle Jr., "Spaceborne observations of the global distribution of carbon monoxide in the middle troposphere during April and October 1994," *Accepted for publication in J. Geophys. Res.*,(1998).

Dianov-Klokov, V.I., "Spectroscopic studies of gaseous pollutants in the atmosphere over large cities", *Izv. Acad. Sci. USSR, Atmos. Oceanic Phys.*, Engl. Transl., **20**, 883-900 (1984).

Dianov-Klokov,V.I., L.N. Yurganov, E.I. Grechko, and A.V. Dzhola, "Spectroscopic measurements of atmospheric carbon monoxide and methane. 1: Latitudinal distribution", *J.Atmos.Chem.,* **8**, 139-151 (1989).

Drummond J. R., G. P. Brasseur, G. R. Davis, J. C. Gille, J. C. McConnell, G. D. Pesket, H. G. Reichle, and N. Roulet, *MOPITT Mission Description Document*, Department of Physics, University of Toronto, Toronto, Ontario, Canada, M5S 1A7, http://www.atmosp.physics. utoronto.ca/mopitt/mdd_93/index.html (1993).

Duggan P., P.M. Sinclair, M.P. LeFlohic. J.W. Forsman, R. Berman, A.D. May, and J.R. Drummond, "Testing the Validity of the Optical Diffusion Coefficient: Line-Shape Measurements of CO Perturbed by N_2," *Phys. Rev. A*, **48**, 2077-2083 (1993).

McKernan, E. P., B. T. Tolton, J. R. Drummond, and L. Yurganov, "MOPITT Validation Using Ground-Based IR Spectroscopy," *SPIE annual general meeting*, this issue (1999).

Novelli, P. C., V. S. Connors, H. G. Reichle, Jr., B. E. Anderson, C. A. M. Brenninkmeijer, E. G. Brunke, B. G. Dodderidge, V. W. J. H. Kirchhoff, K. S. Lam, K. A. Masarie, T. Matsuo, D. D. Parrish, H. E. Scheel, and L. P. Steele, An internally consistent set of globally distributed atmospheric carbon monoxide mixing ratios developed using results from an intercomparison of measurements, *J. Geophys. Res.*, **103**, 19285 - 19293 (1998).

Predoi-Cross A., C. Luo, R. Berman, A.D. May, and J.R. Drummond, "Line Broadening and the Temperature Exponent of the Fundamental Band in CO - N_2 Mixutres," submitted to *J. Mol. Spectrosc.* (1999).

Rothman, L. S., C. P. Rinsland, A. Goldman, S. T. Massie, D. P. Edwards, J. -M. Fluad, A. Perrin, C. Camy-Peyret, V. Dana, J. -Y. Mandin, J. Schroeder, A. McCann, R. R. Gamache, R. B. Wattson, K. Yoshino, K. V. Chance, K. W. Jucks, L. R. Brown, V. Nemtchinov, and P. Varanasi, "The HITRAN Molecular Spectroscopic Database and Hawks (HITRAN Atmospheric Workstation): 1996 Edition," *J. Quant. Spectrosc. Radiat. Transfer*," **60**, 665 - 710 (1998).

Sinclair P. M., P. Duggan, R. Berman, A. D. May, and J.R. Drummond, "Line Broadening, Shifting and Mixing in the Fundamental Band of CO Perturbed by N_2 at 301 K," *J. Mol. Spectrosc.* **181**, 41 - 47 (1997).

Taylor, F.W., "Pressure Modulator Radiometry", *Spectrometric Techniques: Volume III*, Academic Press, New York (1983).

Tolton B. T. and J. R. Drummond, "Characterisation of a Length Modulated Radiometer," *Applied Optics*, **36**, 5409-5420 (1997).

Yurganov, L. N., E. I. Grechko, and A. V. Dzhola, "Zvenigorod Carbon Monoxide Total Column Time Series: 27 Years of Measurements", *Chemosphere*, (in press, 1999).