Multi-Gas analysis of ambient air using FTIR spectroscopy over Mexico City

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RESUMEN

Se utilizó un espectrómetro en el infrarrojo por transformadas de Fourier (FTIR) para analizar la composición de aire ambiente en un sitio de la zona metropolitana de la Ciudad de México. Para ello se introdujo un flujo constante de aire a una celda de gases de paso múltiple y se colectaron los espectros durante un período de dos semanas. Para el análisis cuantitativo, se aplicó el método clásico de mínimos cuadrados (CLS) utilizando espectros sintéticos como referencias y fuentes de calibración. Se observaron patrones interesantes en los niveles ambientales de CO, CO_2, CH_4 y N_2O, los cuales son reportados con una resolución temporal de cinco minutos para el mes de septiembre del 2001. En la evaluación de esta técnica se incluyen comentarios sobre la precisión, los límites de detección, así como de la relación señal/ruido del instrumento. Se estimaron las concentraciones de vapor de agua a través de sus absorciones en el infrarrojo y se compararon los datos con los de un sensor de humedad relativa. La técnica de FTIR por extracción para el monitoreo del aire ambiente fue utilizada por primera vez en México y se sugieren algunas posibles aplicaciones para el futuro.

ABSTRACT

A Fourier Transform Infrared (FTIR) spectrometer was used to analyze the composition of ambient air at a specific site in the Mexico City metropolitan area. A continuous flow of air was passed through a multi-pass gas cell and the absorption spectra were collected over a period of two weeks. Quantitative analysis was performed by means of the classical-least square (CLS) method using synthetically generated spectra as references and calibration sources. Ambient levels of CO, CO_2, CH_4 and N_2O are reported with a time resolution of five minutes for September 2001, showing interesting results in their diurnal patterns. Comments on the precision, detection limits and signal-to-noise of the instrument are included for the evaluation of this technique. Water concentrations were estimated and compared with those obtained with a relative-humidity sensor. The technique of extractive FTIR for ambient trace-gas monitoring was utilized in Mexico for the first time and some potential applications are given.

Key words: FTIR spectroscopy, air monitoring, Mexico City.

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1. Introduction

Mexico City's air quality has become of public concern over the last decade (GDF, 1996; Molina and Molina, 2000; Raga *et al.*, 2001). Large quantities of pollutants are released into the atmosphere through anthropogenic processes such as industry, transportation and services disturbing the natural equilibrium of trace gases through their emissions and thus inducing a complex variety of photochemical reactions (Finlayson-Pitts and Pitts, 2000). As a consequence, human health and ecological issues can be directly affected if no adequate measures are taken to prevent them. Spatial distribution and temporal trend studies provide essential information for inventories, air quality models and to the understanding of atmospheric chemistry. The need for more precise, faster and more versatile gas analyzing systems becomes apparent in such investigations, both in laboratory and field applications.

CO_2, CH_4 and N_2O are among the most important greenhouse gases, which are influenced by human activities. All three gases have both biological and anthropogenic sources and although an increase in the global budget since the Industrial Era has been established, there are sill some uncertainties in the magnitudes of their anthropogenic contribution (IPCC, 2001). Because they have relatively long atmospheric lifetimes, the global interest on the radiative forcing of these gases gains regional and local importance especially when considering the impacts that megacities could play. CO, on the other hand, is important from the tropospheric chemistry point of view. The major source of carbon monoxide is the incomplete combustion of fossil fuels and it is therefore commonly used to monitor the pollution levels particularly in large urban areas (Mayer, 1999).

Fourier Transform Infrared (FTIR) spectroscopy has proven to be a powerful tool for multi-component analysis of gaseous samples. The technique has been used for atmospheric monitoring
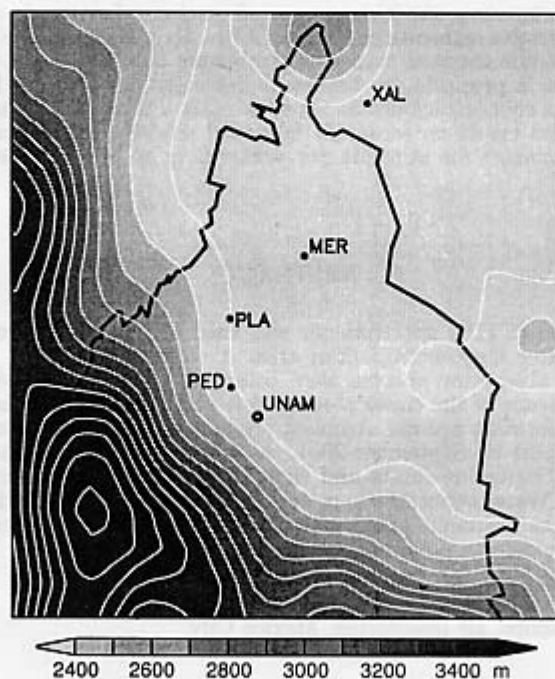

Fig. 1. Location of the measuring site at UNAM, south of Mexico City and other stations from the Automatic Network for Atmospheric Monitoring (RAMA). PED=Pedregal, PLA=Plateros, MER=Merced (downtown), XAL=Xalostoc (north).
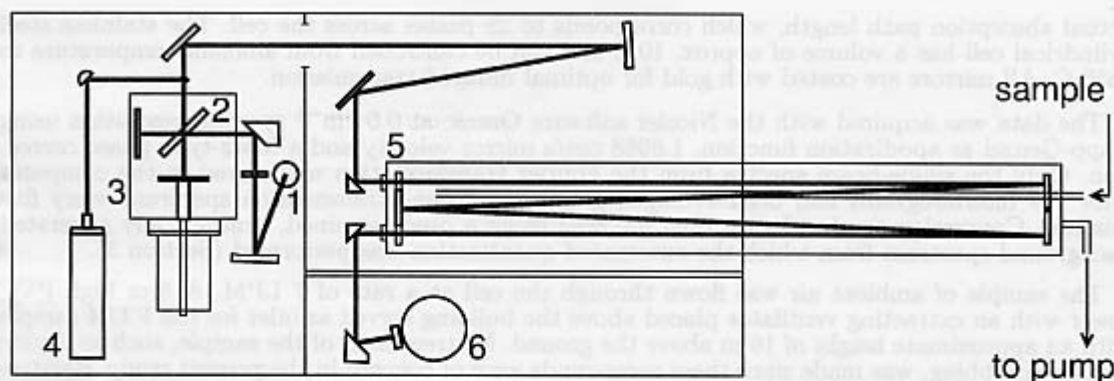
Fig. 2. Schematic of FTIR spectrometer and multi-pass cell. 1 IR source, 2 ZnSe beam-splitter, 3 Michelson interferometer, 4 HeNe laser, 5 White cell < 32m, 6 MCT detector.

by extractive sampling (Beer, 1992; Hanst and Hanst, 1994; Schäfer *et al.*, 1998; Esler *et al.*, 2000) as well as in the open-path configuration (Tuazon *et al.*, 1978; Marshall *et al.*, 1994) for several years. Its worldwide acceptance has motivated its standardization by international agencies (EPA, 1997; ASTM, 1998; VDI, 2000). Other applications include the determination of trace gas fluxes and emission rates using modeling of micrometeorological data (Hargreaves *et al.*, 1996; Schäfer *et al.*, 1998; Hashmonay *et al.*, 1999; Galle *et al.*, 2001; Griffith *et al.*, 2002). It is favored over other spectroscopic techniques for its high selectivity in the infrared region as well as the large averaging capacity as a multiplex system.

In the present study an FTIR spectrometer, coupled with a multi-path "White" cell, has been used to do on-line monitoring of ambient air. The absorption spectra in the infrared region are measured continuously from which the concentrations of several compounds are calculated and reported in an automated fashion. Simultaneous determination of CO, CO_2, CH_4, and N_2O concentrations was achieved with a high sampling frequency (5 min. averaging) and relative errors below 3%. Their temporal profiles are presented as well as a comparison of relative humidity measurements from a conventional sensor and the H_2O concentrations estimated from the absorption spectra.

The measurements were carried out from September 11th to 29th, 2001 at the roof of the Center for Atmospheric Sciences from the National University (UNAM) in Mexico City (19° 19' 37" N, 99° 10'34" W, 2273 masl). The measuring site, located south of metropolitan area, can be seen in Figure 1 together with other main monitoring stations from a network of point sampling sites run by the city government (RAMA). Almost daily afternoon rains and relatively low pollution levels compared to other seasons can characterize the sampling period in the region.

2.   Experimental Section

A schematic of the instrument used for multi-gas analysis is shown in Figure 2. Both the base FTIR unit and the cell accessory were constructed by Industrial Monitor and Control Corporation (IMACC). It consists of a commercially available Nicolet Nexus interferometer with a maximum unapodized resolution of 0.125 cm^{-1}, a glowbar infrared source, a ZnSe beamsplitter and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The operating spectral range is approx. 600-4000 cm^{-1}.

The gas cell has a "White" type mirror configuration (White, 1942) for variable paths and a maximum optical length of 32 m. All measurements for this contribution were obtained at 22.86 m

actual absorption path length, which corresponds to 28 passes across the cell. The stainless steel cylindrical cell has a volume of approx. 10 L and can be controlled from ambient temperature to 185° C. All mirrors are coated with gold for optimal infrared transmission.

The data was acquired with the Nicolet software Omnic at 0.5 cm^{-1} spectral resolution using Happ-Genzel as apodization function, 1.8988 cm/s mirror velocity and a Merz-type phase correction. Only the single-beam spectra from the Fourier transformation was stored in the computer after 179 interferograms had been averaged giving rise to one transmission spectrum every five minutes. Conversion to absorbance then followed using a predetermined, synthetically generated background spectrum from which the automated quantization was performed (Section 3).

The sample of ambient air was flown through the cell at a rate of 7 LPM. A 5 m high PVC tower with an extracting ventilator placed above the building served as inlet for the FTIR sample with an approximate height of 16 m above the ground. No treatment of the sample, such as drying or CO_2-scrubbing, was made since these compounds were of concern in the present study. Relative humidity (HMP45D) and temperature (RTD, PT100) sensors from Vaisala were installed in the vicinity of the sample inlet. Additional sensors inside the cell were used to monitor the pressure and temperature.

3. Quantitative analysis

The analytical method used to determine the individual concentrations in the recorded spectra was following the classical-least-square CLS procedure (Haaland et al., 1985). This technique has been widely used for analysis in FTIR and other applications because of its speed and simplicity (Hart and Griffiths, 2000; Esler et al., 2000; Spellicy, 2000). There are nevertheless, several things that could affect the analysis when doing CLS and need to be accounted for. These are therefore explained below in some detail.

In principle, a synthetically generated background spectrum is created prior to the measurements that will, in a good approximation, simulate I_o in Beer-Lambert's law. The conversion to absorbance is done with the same background spectrum for all the successive measurements assuming that they fall in a given signal range. The absorbance spectra are then corrected for line shifts using several lines in the H_2O or HDO reference spectra, depending on the water vapor concentrations. This step is important since it reduces errors in the CLS regression that can be due to instrumental effects or changes in the atmospheric conditions.

The CLS analysis is performed separately for the compounds of interest. The spectral windows are chosen taking into account two basic criteria: absorption coefficients and interferences with other absorbing species in that region. In the case of the less abundant/absorbing compounds (i.e. CO, N_2O, and CH_4) one looks for regions where the absorption peaks are the strongest and the overlap with interfering compounds is minimal. On the other hand, compounds which at normal

Table 1. Spectral windows, the corresponding transition types and interfering species considered for each compound in the CLS analysis.

Compound	Spectral Region [cm^{-1}]	Transition	Interferences
CO_2	723–766	ν_2 ; scissoring	H_2O
H_2O	830–1130	ν_2 ; bending	CO_2
CO	2109–2178	ν_{CO} ; P-branch	H_2O, CO_2, N_2O
N_2O	2188–2224	ν_3 ; N-N asym. str.	H_2O, CO_2, CO
CH_4	2894–3001	ν_3 ; C-H asym. str.	H_2O

atmospheric concentrations and increased path-lengths present total absorbing regions, such as water and carbon dioxide, need to be treated differently.

The residual is the resulting spectrum after all the references have been subtracted from the sample spectrum by the CLS regression. It is useful in choosing those spectral windows where the variations, and hence the error bars, are the smallest. Table 1 shows the spectral regions used for the quantification of the compounds analyzed as well as the corresponding type of vibrational transition involved. The above steps are performed at near real-time by the program GetConcs from IMACC, which runs simultaneously to the data acquisition software.

Calibration and Reference Spectra

Own-measured spectra for each compound can be used as references provided that good accuracy in the concentration is attainable. Another possibility is to use spectra from the various infrared libraries commercially available. Since none of these which would adequately match the observed spectra were available, a third possibility was exploited: reference spectra were generated synthetically for all of the compounds considered in this work using the HITRAN database (Rothman *et al.*, 1998). In doing this, it is important that a good algorithm is employed to simulate the instrumental line-shapes and thus match the measurement parameters as close as possible. The E-Trans code (SpectraSoft Technology, USA) served this purpose since it can manage different spectral resolutions, use a variety of apodization functions and define the data point spacing to equate that of the measured spectra. Moreover, the computed infrared spectrum is generated at a specific value of temperature and pressure according to the atmospheric conditions.
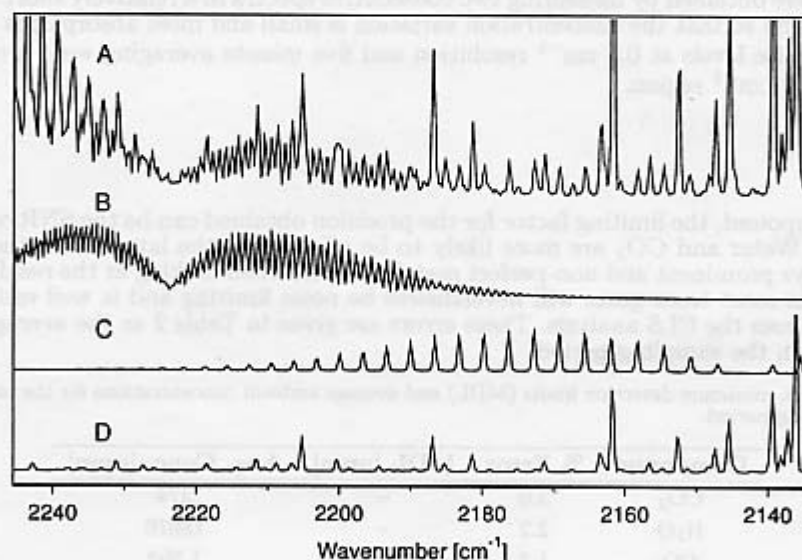

Fig. 3. FTIR spectral window showing: **A** one sample spectrum and **B** N_2O, **C** CO and **D** H_2O reference spectra computed with E-Trans.

In Figure 3, a spectral region is shown where a portion of the sample spectrum is displayed together with the synthetic spectra generated for N_2O, CO and H_2O. As a control procedure for the accuracy of the method, manual quantification by subtraction and scaling was made in several cases giving good agreements with the CLS results.

Non-Linearity

Gas concentration and absorption strength are in principle linear, but this is only true for infinitesimal concentrations. It is well known that non-linearity increases with the partial pressure of the analyzed gas but it is not its only source. Non-linearity is a multiple effect (Spellicy, 2000). An important contribution in this application is the HgCdTe detector, which is inherently non-linear but can, for the most part, be corrected by its amplifier. There could also be non-linearity from finite resolution. If the instrument has a spectral resolution of 0.5 cm^{-1} but the absorption lines of the absorber are narrower, the linearity can be significantly affected. The CLS procedure needs therefore a correction that can be implemented in the software.

A non-linearity correction was done for water vapor, which has the strongest absorptions in the spectrum. Several synthetic spectra were generated at different concentrations in the 0.5 - 2.5% H_2O range and a quadratic fit was used to correct the reported values. The other gases showed no significant non-linearity except for CO, for which a correction was also included.

Signal-to-Noise Ratio

One thing that needs to be considered when evaluating the quality of the spectra is the signal-to-noise ratio (SNR). It is mostly an instrumental limitation, which can partially be overcome by the averaging time. Also, the higher the resolution the lower the SNR becomes and therefore a tradeoff between spectral resolution and averaging time exists. One has to consider as well that increasing the resolution will improve the selectivity, compromising the noise levels at the same time. SNR is conveniently reported as the root-mean-squared (RMS) of equivalently absorbance spectra (EPA, 1997). These were obtained by measuring two consecutive spectra in a relatively short time, treating one as background so that the concentration variation is small and most absorptions are cancelled. Typical RMS noise levels at 0.5 cm^{-1} resolution and five minute averaging were around 5×10^{-5} A.U. in the 2500 cm^{-1} region.

Precision

For each compound, the limiting factor for the precision obtained can be the SNR or its deviation from linearity. Water and CO_2 are more likely to be affected by the latter since their absorption bands are always prominent and non-perfect matches result when looking at the residual spectrum. The precision in most trace gases will nevertheless be noise limiting and is well estimated by the error reported from the CLS analysis. These errors are given in Table 2 as the average uncertainty of the analysis in the sampling period.

Table 2. CLS errors, minimum detection limits (MDL) and average ambient concentrations for the target compounds during the sampling period.

Compound	% Error	MDL [ppm]	Avg. Conc. [ppm]
CO_2	3.0	–	374
H_2O	2.2	–	18070
CO	1.3	0.013	1.392
N_2O	1.5	0.003	0.331
CH_4	2.7	0.024	2.340

Water interferes in basically all analytical windows (Table 1), and its residues affect the errors of the other gases by different magnitudes. The precision in the analysis could therefore be considerably improved if the water were removed from the sample compartment. Using a measured spectrum as water reference would also produce cleaner residuals and hence smaller errors.

Detection Limits

The minimum detection limits (MDL) of the compounds analyzed with FTIR spectrometry depend on the infrared absorption coefficients, the optical path length, the sensitivity of the instrument and its SNR levels. This quantity may vary considerably if the concentrations of the target gas and interfering species change. SNR usually sets the lower limit of detection.

The MDLs reported in Table 2 were calculated according to the Compendium Method TO-16 (EPA, 1997). Basically, 16 single beam spectra are taken in which the concentrations of the target compounds present minimal variations. Their absorbance spectra are then created using the consecutive spectra as backgrounds. MDL is taken as three times the standard deviation from the analytical results within this particular data set.

4. Results and Discussion

Carbon Monoxide

Several rovibrational lines from the infrared spectrum of CO, partially shown in Figure 3c, were used for its quantization. The resulting carbon monoxide concentrations from the first week of the sampling period are presented on the top of Figure 4. As mentioned earlier, the accuracy of these values, as well as for the other compounds, was tested manually using the references generated with the HITRAN line parameter set (Rothman et al., 1998). The average uncertainty from the CLS regression was 1.3% (Table 2) .
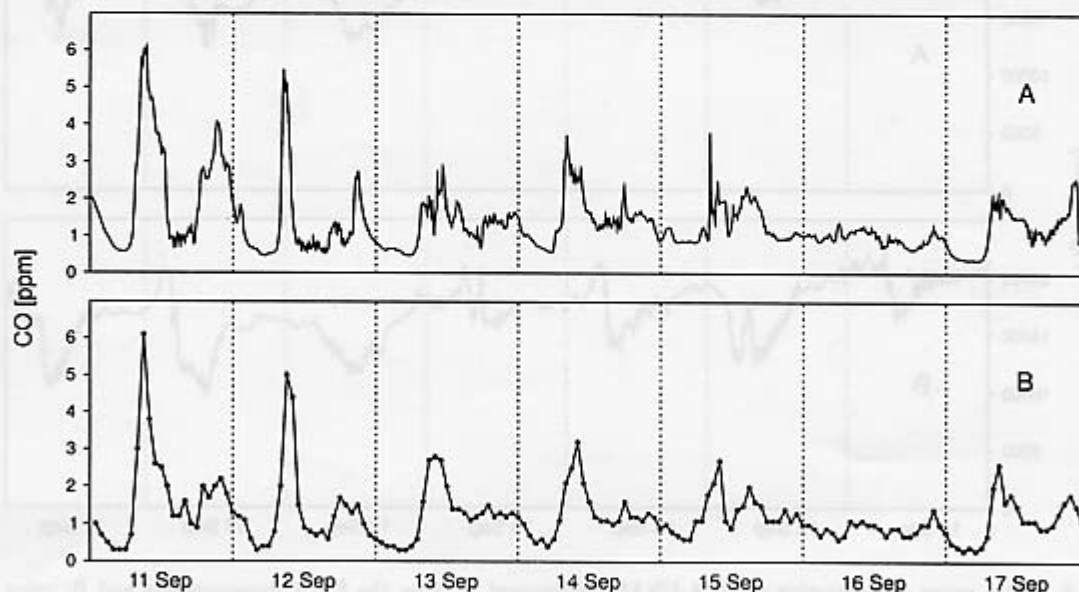

Fig. 4. A: FTIR determination of CO concentration every 5 minutes at CCA - UNAM. B: Hourly measurements of CO at the monitoring station in Plateros (PLA).

The daily patterns of peak emissions during the morning (average peak hour 8:34) and the afternoon (20:28) are evident in all working days and is almost absent on Sunday (Sep 16th), as expected from vehicular activities. For comparison, data obtained from a CO analyzer in a close-by monitoring station is included at the bottom of Figure 4. There is clear resemblance in the

curves although the Plateros monitoring station is 5.3 Km from the measuring site (UNAM). We can observe from Figure 1 that the Pedregal station is closer to the measurement site although less resemblance was found with it. The PED site is located in a residential area with uneven topography and with more green areas than in the great urban region to the north, were the wind is predominately coming from. From this comparison it can be deduced that given the local nature and the relatively long lifetime of this pollutant, the daily CO profiles will be in general well distributed throughout the city and will be ruled by the prevailing wind patterns of the region.

Water Vapor

Since water is the largest interference in the quantification of the other trace gases considered, it is interesting to determine how well the analytical method is doing in reporting its concentration. The region between 830 and 1130 cm^{-1} was chosen because its rotational lines are not excessively intensive but still with absorbance values appropriate for analytical treatment. The reference spectra was created at 20'000 ppm (or 2% mixing ratio at 590 Torr) and a non-linearity correction was applied based on spectra at five different concentrations covering a larger range than the measured one.
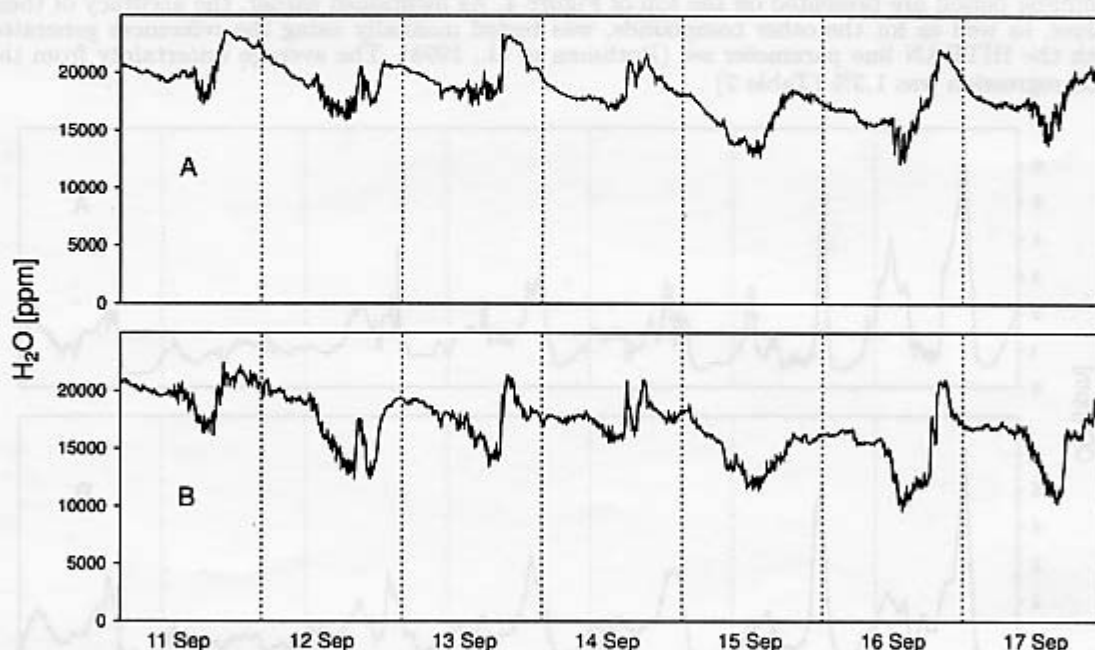

Fig. 5. Water vapor concentration at CCA-UNAM determined A: from the FTIR measurements and B: using a relative humidity sensor (at 587 Torr and variable temperature).

In Figure 5 the water vapor concentration of a 7-day period is presented. The curve on the top results from the CLS calculation of the corrected FTIR data. The values collected from the humidity sensor needed some treatment in order to be converted from relative humidity to the desired mixing ratio. This is done by determining the saturation partial pressure of water at the measured temperature, fractioning it from the reported relative humidity value to obtain the actual partial pressure of water and finally, expressing it as a mixing ratio (%, ppm, ppb, . . .) at the

desired atmospheric pressure. Values obtained from the relative humidity sensor at an average pressure of 587 Torr are displayed in the bottom part of Figure 5 for comparison purposes. In general, there is a good agreement between the two methods.

N_2O and CH_4

Nitrous oxide and methane from ambient air are readily observed in the infrared spectrum. Their concentrations for one week at the UNAM site are presented in Figure 6. The average error and minimum detection limit were estimated at 1.5% and 3 ppb for N_2O, respectively. CH_4 showed somewhat larger values for the errors and MDL as can be seen in Table 2; namely 2.7% and 24 ppb, respectively.
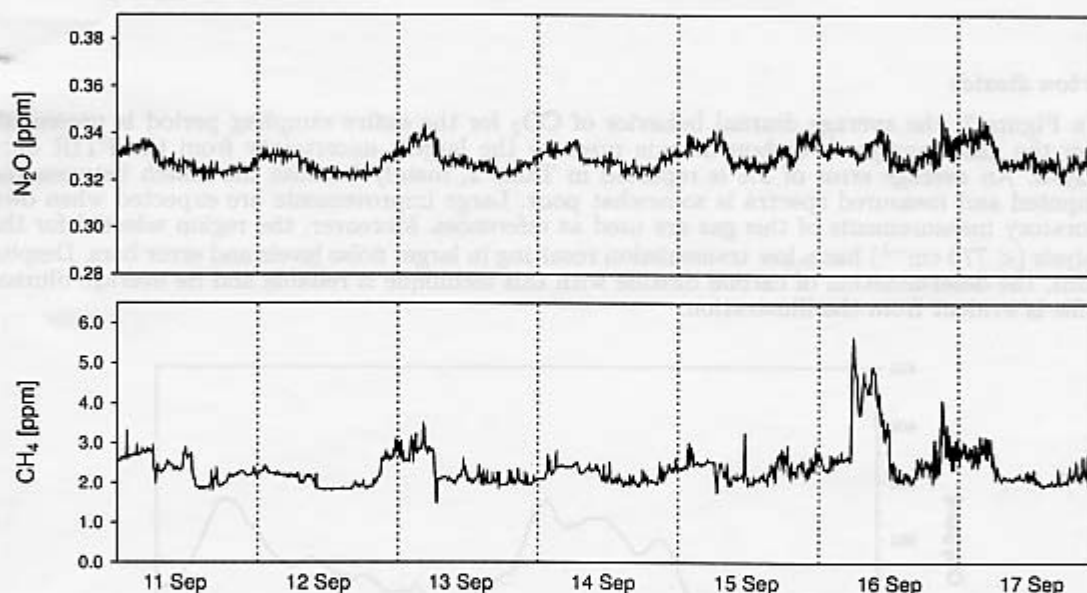

Fig. 6. N_2O and CH_4 concentration curves for September 2001 measured with the FTIR and multi-pass White cell (~ 23 m). Dotted lines correspond to midnight hours.

The large and sporadic variation in the methane concentrations as opposed to that of nitrous oxide is an indication that CH_4 is more influenced by anthropogenic emissions than N_2O. It has been estimated that slightly more than half of current methane emissions are anthropogenic, whereas for N_2O the estimate lies at around one third (IPCC, 2001). This difference should be more apparent around urban areas. It is evident from the illustration that the persistent and narrow peaks throughout the week do not originate from natural sources, particularly during the intense event on September 16th. An important source for methane in Mexico City and other large cities is known to be the gas leakages, although sanitary landfills, animal wastes and biomass burning need also to be taken into consideration. The observed average at 2.34 ppm in Mexico City (Table 2) for this period is considerably higher than the reported global average of 1.76 ppm (IPCC, 2001).

The nitrous oxide concentrations are less sensitive to local changes as can be observed from the figure. Nevertheless, a correlation between the low variational behavior of the CH_4 and N_2O curves can be established. This diurnal fluctuation has maxima during the night hours and decreases slightly throughout the daytime for both compounds. The contribution of anthropogenic processes

for N_2O emissions is mainly from agricultural soils, sewage treatment and fossil fuel burning (e.g. chemical industry and vehicle engines when cold started). The observed average concentration, which was 0.331 ppm for the period in this study, is again higher than the reported background concentration at 0.316 ppm (IPCC, 2001).

The fact that the turning points for the low variations in the diurnal behavior of CH_4 and N_2O are occurring every day at the same times and that their lifetimes are sufficiently long, offers an indication that their behavior is related to the regional wind patterns. It has been stated that the prevailing winds for the rainy season in this part of the city come from the south-west during the night and arrive more intensively from the north and north-east during daylight hours (Klaus *et al.*, 1999). This valley-to-basin flow pattern has been confirmed (Doran *et al.*, 1998) and is possibly a drainage flow of compounds like these from the mountainous and more vegetated areas to the south and to the west of the measuring site.

Carbon dioxide

In Figure 7, the average diurnal behavior of CO_2 for the entire sampling period is presented. From the gases analyzed, carbon dioxide presents the largest uncertainty from the FTIR data analysis. An average error of 3% is reported in Table 2, mainly because the match between the computed and measured spectra is somewhat poor. Large improvements are expected when own laboratory measurements of this gas are used as references. Moreover, the region selected for the analysis (< 770 cm^{-1}) has a low transmission resulting in larger noise levels and error bars. Despite of this, the determination of carbon dioxide with this technique is reliable and its average diurnal profile is evident from the illustration.
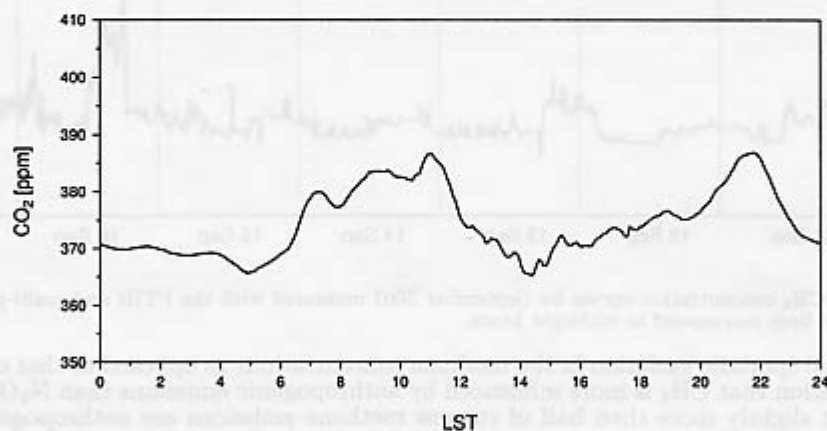

Fig. 7. Hourly CO_2 concentration at UNAM as an average of the two week period between the 11th and the 29th of September, 2001.

Aside from a study during 1981 to 1982 in which CO_2 was measured to observe the annual patterns and its diurnal relationship to pollution levels in Mexico City (Baez *et al.*, 1988), no additional investigations were found in the literature for the area of study. The atmospheric concentration of carbon dioxide has increased by 31% since 1750 mainly due to fossil fuel burning and deforestation. During the 1990's the year-to-year increase varied between 0.9 and 2.8 ppm and the current CO_2 value lies around 360 ppm (IPCC, 2001). The average concentration in this work (374 ppm) is larger than the global mean as is expected in urban areas. The observed average profile in Figure 7 depicts a large diurnal variability caused primarily by automotive emissions. Two

prominent emission features that support this statement appear during the morning and evening hours and occur more evidently during working days.

5. Conclusions

The present contribution has shown that FTIR spectroscopy is a reliable technique for ambient air monitoring owning the following advantages: multi-component analysis with one instrument, on-line report of concentrations, high acquisition frequency and precision, low maintenance and operation, reliability, etc. This last property gains its significance from the fact that post-analysis of the data is possible to verify and control the reported results as in the case of the sudden presence of a large interference not considered by the running method, or sweeping changes in the atmospheric conditions.

Accurate diurnal profiles for the greenhouse gases CH_4, N_2O and CO_2 were obtained with high acquisition frequencies. These constitute the most detailed temporal structures found in the literature for the Mexico City metropolitan area providing a valuable insight in the possible origins and anthropogenic contributions for these gases. The background concentrations for the September 11th - 29th, 2001 period were 2.34, 0.331 and 374 ppm, respectively. Carbon monoxide was measured with an average analytical uncertainty of 1.3% and its temporal profile was successfully compared to that of a monitoring station approx. 5 km to the north.

It has been pointed out that error improvements in the reported concentrations can be accomplished using own-measured spectra calibrated with the HITRAN-based computed references. The results on water vapor were in good agreement with the relative humidity values although in the future, the latter information could aid the analytical method in determining what spectral region to use according to the amount of water present in the sample. The sensitivity and signal-to-noise of other gases can thus be further improved if water is partially removed from the sample inlet.

Potential applications for future FTIR studies include the open-path configuration. In this technique the infrared beam, guided by two facing telescopes, traverses the atmosphere horizontally 100 - 500 meters near the surface allowing for better sensitivities and the interrogation of a larger variety of gaseous compounds through increased optical paths of a non-perturbed sampling system. A speciation of this kind has only been achieved in campaigns involving several conventional analyzers and other sampling techniques in the region, which in turn cannot always provide a continuous measurement cycle. Such investigations are already under way in downtown Mexico City. Also, the multi-pass cell in conjunction with simple sample-handling techniques can lead to detailed speciation studies of specific emission sources such as engine exhausts or industrial plumes.

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