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Abstract. Carbon dioxide (CO_2) is one of the most important long-lived anthropogenic greenhouse gases. Ocean, land and biosphere contribute to take up CO_2 emissions, but approximately half of fossil fuel CO_2 accumulates in the atmosphere. The study of isotopic composition of CO_2 can give useful information for assessing and quantifying the uptake of CO_2 in the environmental compartments, as well as for distinguishing natural from anthropogenic carbon in the atmosphere. In this work, an activity for the development of a Fourier Transform Infrared spectroscopy (FTIR) based method for $\delta^{13}C$-CO_2 determination in CO_2 in air mixtures is presented. The FTIR can be calibrated by a classical approach based on primary calibration gas standards, but an alternative calibration can be based on the generation of synthetic spectra, by means of radiative transfer calculation codes such as the Multiple Atmospheric Layer Transmission (MALT - University of Wollongong, Australia). Another software (B-FOS) developed at the *Bureau International des Poids et Mesures* (BIPM) allows to interface MALT and the FTIR management software. This calibration approach is fast and reliable and can be used when the classical calibration based on reference gas mixtures might be demanding. The uncertainty obtained for $\delta^{13}C$-CO_2 measurements is around 0.1 ‰, at a nominal CO_2 mole fraction of 400 μmol mol^{-1} in air.

1 Introduction

Carbon dioxide (CO_2) is one of the most important long-lived anthropogenic greenhouse gases. Ocean, land and biosphere contribute to take up CO_2 emissions, but approximately half of fossil fuel CO_2 accumulates in the atmosphere. The study of isotopic composition of CO_2 can give useful information for assessing and quantifying the uptake of CO_2 in the environmental compartments, as well as for distinguishing natural from anthropogenic carbon in the atmosphere. Carbon has two naturally occurring stable isotopes, ^{12}C and ^{13}C, with abundances of 98.89 % and 1.11 %, respectively (with the naturally occurring radioisotope $^{14}C < 10^{-10}$ %). CO_2 exists in 12 stable isotopometric forms, since there are also three stable oxygen isotopes ^{16}O, ^{17}O, and ^{18}O.

Isotope ratios are usually expressed relative to some accepted standard in the “delta” (δ) notation, for example:

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$$\delta^{13}\mathrm{C} = \left[\left(R^{13}_{\mathrm{sample}}/R^{13}_{\mathrm{standard}}\right) - 1\right] \times 1000 \quad (1)$$

where R^{13} = $^{13}C/^{12}C$ is the ratio of the abundances of ^{13}C and ^{12}C. The δ values are expressed in the units of ‰ (per mil).

For $\delta^{13}C\text{-}CO_2$, the conventional reference standard is the VPDB scale (Vienna Pee Dee Belemnite) maintained by the International Atomic Energy Agency. The $\delta^{13}C_{VPDB}$ value of a material describes how far the isotope ratio in that material differs from the ratio in the standard [1].

In this work, the activity carried out at INRIM for the development of a Fourier Transform Infrared spectroscopy (FTIR) based method for $\delta^{13}C\text{-}CO_2$ determination in CO_2 in air mixtures is described. This activity is carried out in the framework of the EMPIR Project 16ENV06 "Metrology for Stable Isotope Reference Standards" (SIRS) [2].

1.1 CO_2 carbon stable isotope ratios measurement by FTIR

Alternatively to the classical calibration approach based on the use of reference gas mixtures, the FTIR spectrometer can be calibrated by means of synthetic spectra generated by a radiative transfer calculation code named MALT, acronym for Multiple Atmospheric Layer Transmission, developed at the University of Wollongong (Australia). MALT uses the HITRAN database spectral lines to generate synthetic infrared spectra of gas phase mixtures. Another software (B-FOS) developed at the *Bureau International des Poids et Mesures* (BIPM) can be used to interface MALT and the software of the FTIR (Thermo Fisher Scientific Omnic®). This approach is fast and reliable and can be used when the classical calibration based on reference gas mixtures might be demanding in terms of time and gas consumption.

The presented calibration procedure, adapted from BIPM [3], is based on the use of two CO_2 standards of different mole fraction but similar isotopic values, for the bracketing of unknown samples. Two major isotopologues of CO_2, 626 ($^{12}C^{16}O^{16}O$) and 636 ($^{13}C^{16}O^{16}O$) are determined, in two different spectroscopic regions (3500-3800 cm^{-1} for 626 and 2200-2300 cm^{-1} for 636). The uncertainty associated with the $\delta^{13}C$ measurements takes into account several contributions, e.g. the stability of the FTIR, the HITRAN uncertainty for the CO_2 line parameters and the uncertainty of the regression algorithm, based on classical least squares (CLS), used by MALT. The uncertainty for $\delta^{13}C\text{-}CO_2$ measurements is around 0.1 ‰, at a nominal CO_2 mole fraction of 400 μmol mol^{-1} in air.

1.2 FTIR spectroscopy

The FTIR spectroscopy is based on the Beer-Lambert Law, which defines the transmittance $T(\nu)$ of a sample at wavenumber ν as the ratio of the radiant power emerging from the rear face of the sample at that wavenumber $I(\nu)$ to the power of the radiation at the front face of the sample, $I_0(\nu)$:

$$T(\nu) = I(\nu)/I_0(\nu) = \exp[-\alpha(\nu)b] \quad (2)$$

where $\alpha(\nu)$ is the linear absorption coefficient (cm^{-1}) at ν.

The absorbance of the sample at ν, $A(\nu)$, is given by the base 10 logarithm of $1/T(\nu)$. If the sample is a mixture, the absorbance of each i-*th* component at a concentration c_i, is given by the Beer's Law as:

$$A_i(\nu) = \log_{10}(1/T(\nu)) = a_i(\nu)bc_i \quad (3)$$

where $a_i(v)$ has the unit (concentration·path·length)$^{-1}$.

A FTIR spectrometer usually consists of 5 parts: the infrared source, the mirrors (a moving mirror and a fixed mirror), the beam splitter, the sample cell and the detector.

The infrared absorption spectroscopy is performed by directing an infrared beam through a sample to a detector. The molecules with a permanent dipole in a sample absorb the infrared radiation and the absorbance occurs in a characteristic and reproducible pattern. First, an interferogram is formed, and then the single beam spectrum is obtained through the Fourier Transform.

The absorbance spectrum is generated by the FTIR in subsequent steps: 1) the single beam spectrum of the background is recorded via Fourier Transform of the interferogram; 2) the single beam spectrum of the sample is also recorded via Fourier Transform of the interferogram; 3) the transmittance spectrum is calculated as the ratio of the single beam spectra of the sample and the background via software; 4) the absorbance spectrum is formed by calculating ($-\log_{10}$) of the transmittance spectrum via software.

The FTIR spectrometer used at INRIM is a Thermo Fisher Scientific Nicolet iS50, equipped with a 10 m gas cell, shown in fig. 1.

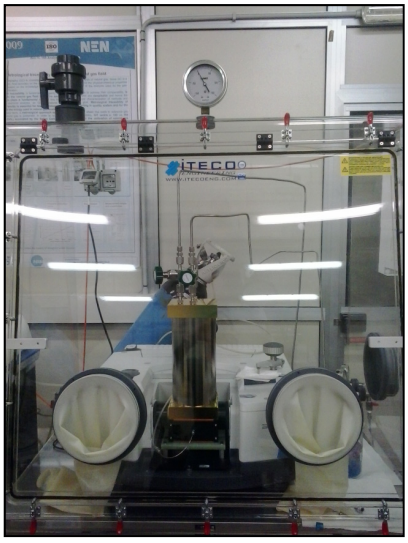

Fig. 1. INRIM's FTIR spectrometer (Thermo Fisher Scientific Nicolet iS50), equipped with a 10 m gas cell.

2 Calibration procedure

2.1 Software used

MALT is a radiative transfer calculation code developed at the University of Wollongong (Australia), which can generate synthetic infrared calibration spectra of gas phase mixtures. These calibration spectra are calculated from a database of absorption line parameters, called HITRAN.

MALT calculates atmospheric transmission or absorbance spectra and then modifies the ideal spectra to take into account different effects that occur in the real spectrometers. These include both environmental (e.g pressure, temperature, path length) and instrumental (e.g resolution, line shape, wavenumber shift) effects, and they are taken into account in the software calculations, to obtain spectra that closely approximate real measured spectra [4].

MALT is used together with another software, named B-FOS, which is a LabView-based software able to interface the FTIR software (e.g Thermo Fisher Scientific Omnic®), necessary to control the FTIR spectrometer, and MALT. In figure 2, the interface of B-FOS is shown, with the typical measured and fitted spectra of CO_2 (lower part) and residual signal (upper part) in the region (3500−3800) cm^{-1}.

HITRAN is the acronym for High-Resolution Transmission Molecular Absorption Database. This database is a compilation of spectroscopic parameters including over one million spectral lines of 49 molecules and their isotopologues. These parameters can be used to predict and simulate the transmission and emission of light in the atmosphere. This database was started in the late 1960s in response to the need for detailed knowledge of the infrared properties of the atmosphere. HITRAN includes several information, among which the line-by-line spectroscopic parameters for high-resolution molecular absorption and radiance calculations, and infrared absorption cross-sections.

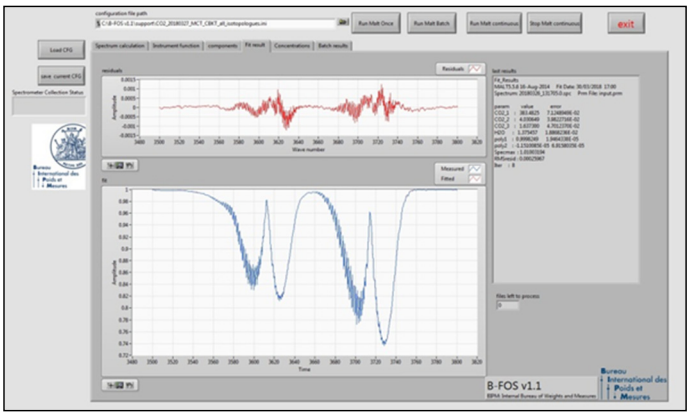

Fig. 2. Typical measured and fitted spectra (lower part) and residual signal (upper part) in the region (3500−3800) cm^{-1} obtained for CO_2 (Courtesy of BIPM).

2.2 Calibration procedure with synthetic spectra

The first step when setting up a FTIR method for the quantification of gas analytes, such as CO_2, based on the calibration of the instrument by means of synthetic spectra is the set-up of the fitting parameters, to be used by the MALT software. The spectral region to be analysed is iteratively calculated and fitted to the measured spectrum by CLS regression. From the HITRAN line parameters, MALT calculates the absorption coefficients of the gas sample in the FTIR measurement cell, at the measured temperature and pressure. The monochromatic transmittance spectrum is calculated from the absorption coefficients and initial estimates of trace gas concentrations (e.g. water vapour), then is convolved with the FTIR instrument line-shape function (ILS), which includes the effects of parameters such as the resolution (maximum optical path difference of the interferogram), the apodization, and the finite field of view (beam divergence in the interferometer). The resulting calculated spectrum simulates the measured spectrum and is iteratively re-calculated until the best fit (minimum sum of squared residuals between measured and calculated spectra) is achieved [5]. Through B-FOS, the synthetic spectrum can be produced by MALT and then fitted to the measured spectrum by adjusting various parameters.

The spectral region (2200-2300) cm^{-1} shows a peak of high intensity, typical of the CO_2 isotopologues 626 and 636, but the (3500-3800) cm^{-1} region is preferred for the quantification of the most abundant 626 isotopologue, due to the lower intensity of the signal in this region.

The water vapour must be fitted in all spectral regions, because there are weak residual water vapour lines even in dried air. In the region near to 2300 cm^{-1}, the ^{13}C and ^{12}C isotopologues of CO_2 are well resolved and can be fitted independently, allowing direct measurement of ^{13}C in the CO_2 mixtures.

Another important step to evaluate the performance of the FTIR spectrometer, is the calculation of the short-term noise of the instrument, which can be carried out by analising continuously a CO_2 in air reference mixture (around 400 µmol/mol) and then by calculating the Allan variance of the repeated measurements.

From the plot of the Allan variance, the best averaging time of the instrument can be evaluated, determining the optimal scanning time of FTIR (typically 4-5 min).

In fig. 3, a CO_2 spectrum is reported, showing the two regions typical of the IR absorption of this molecule.

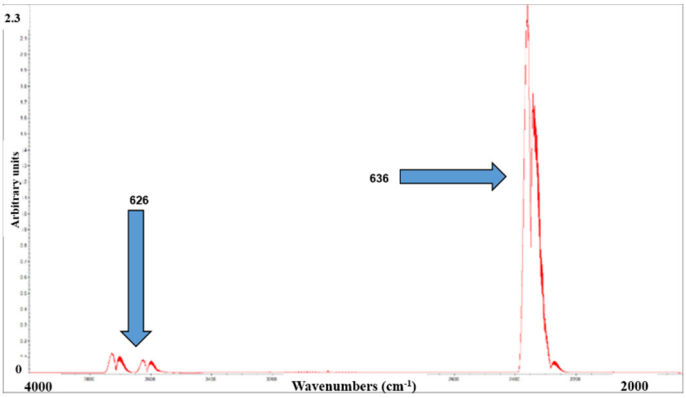

Fig. 3. CO_2 spectrum, showing the two regions typical of the IR absorption of this molecule, (3500-3800) cm^{-1} on the left and (2200-2300) cm^{-1} on the right.

The calibration procedure for the analysis of the isotopic composition of CO_2 in air standards by means of FTIR is derived from [3]. The procedure is based on the calibration of the instrument responses to the individual 626 and 636 isotopologues. The theoretical mole fraction of each individual isotopologue in two standards of known CO_2 mole fractions and isotopic composition are calculated. This is done by first calculating the atomic isotopic abundances X in each of the calibration gas mixtures. Then each CO_2 isotopologue mole fraction in the reference gas is calculated according to its composition. These theoretical reference isotopologue mole fractions are plotted versus the mole fractions generated by MALT from the FTIR measurements, to determine two calibration equations, one for each isotopologue.

The calibration curves are established to ensure that the isotopologue mole fractions in the two calibration standards bracket the isotopologue mole fractions in the unknown mixtures. The predicted mole fractions of the isotopologue in an unknown sample were calculated from the corresponding calibration equation. In the last step, the calibrated responses were used to determine the isotope ratios of the measured sample and, finally, the $\delta^{13}C$ values of the unknown mixture, following equation (1).

2.3 Uncertainty evaluation

For the FTIR uncertainty evaluation, the approach described in [6] was applied to the determination of the mole fractions and isotopic deltas of CO_2 in air gravimetric standards.

When performing a synthetic calibration there is not a simple equation giving the mole fraction, and the evaluation of the uncertainties by applying the law of propagation of uncertainty, recommended in the GUM, cannot be straightforward. As a first approach, some input quantities were taken into account such as:
- The stability of the FTIR obtained from the noise analysis;
- The uncertainty for the CO_2 line parameters, derived from the HITRAN database of molecular parameters;
- The uncertainty from MALT CLS regression.

The uncertainty from MALT CLS can be carried out by evaluating the uncertainties in the experimental and calculation parameters, among which path length, temperature, amount of the analytes, number of half-widths, resolution, collimator aperture, pressure, asymmetry in the line shape, wavenumber shift related to HITRAN, line broadening.
The combined standard uncertainty associated with the FTIR measurements is the following:

$$u_{CO2} = \sqrt{(u_{noise})^2 + (u_{HITRAN})^2 + \left(u_{calcMALT\_CO2}\right)^2} \quad (4)$$

3 Conclusions

The possibility to discriminate anthropic from natural contributions in the atmosphere of the main greenhouse gases, as CO_2, by determining their isotopic composition relying on metrologically-sound reference standards is crucial to improve the understanding of the global carbon cycle and the sources and sinks of greenhouse gases in the atmosphere.
The presented approach offers a possible alternative to the classical calibration of the FTIR spectrometer by means of several reference gas mixtures, as this procedure might be time and gas consuming.

Further developments to this work will focus, in particular, on the optimisation of an automatized sampling and measurement system and on the investigation of other relevant sources of uncertainty, to lower the final uncertainty of $\delta^{13}C\text{-}CO_2$ measurement results.

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