

The use of FTIR analysis in determining the purity of gases

Miroslava Valková^a, Viliam Pätoprstý^a, Michael Lawson^b

^a*Centre of Chemistry, Slovak Institute of Metrology, SK-84255 Bratislava, Slovakia*

^b*Faculty of Chemical and Food Technology, Slovak Technical University,
SK-812 37 Bratislava, Slovakia*

michael.lawson@stuba.sk

Abstract

In this paper we report the use of FT-IR spectroscopy in the determination of purity of gases. The FT-IR spectroscopy was adopted to evaluate the limit of detection for carbon dioxide, carbon monoxide and water. The experimental details of the measurements, detection limit and other considerations are discussed in more detail.

Keywords: FT-IR spectroscopy, purity of gases, limit of detection

Introduction

Spectral properties of gases are significantly different from samples in the condensed phase (Milata et al., 2008; Halland 1990). The main difference stems from the low density of the gas. For gaseous samples, it is typical that in the spectrum are well observable, in addition to vibrations, also rotational transitions (Chu et al., 1999). The great advantage of gas samples is that their spectra are resistant to impact and matrices are simply the sum of the individual components. Wavelengths of spectral bands do not shift due to the environmental coupling. Both these properties are due to the low gas density and consequently very low influence of surrounding gas molecules (Bak and Larsen, 1995). This paper reports on the determination of the purity of the primary reference gas materials using FT-IR spectroscopy.

Experimental

For the determination of gas impurity a FT-IR Bomem MB 100 spectrometer was used, equipped with DTGS (deuterated triglycine sulfate) detector. This allows spectra in the Mid - IR 400-4000 cm^{-1} to be obtained. The spectrometer is equipped with a cell with optical paths

of 10 meters. Cell design uses multiple reflection of infrared beam inside the cell. To achieve the 10 m optical path, the radiation is completely reflected 20-times in the cell which is 50 cm long. To ensure optimum reflection of radiation, gold mirrors are used. Although the reflective surface of the gold is lower than that of silver, gold is preferred mainly because of its corrosion resistance. The volume of the cell with a 10 m optical path is 2 liters. The body of the cell is made of glass, can be evacuated and can be used up to a 200 kPa pressure. Above that a pressure relief valve is opened and the content of the cell is automatically released into the environment. To measure the background spectrum, the cell is evacuated, usually to a pressure value of about 10^{-5} mbar. All experiments were performed at 22 °C.

Decrease in the limit of detection is dependent on the reduction of noise level (Cleaver, 2001). Noise level is a function of the intensity of the source, the number of scans, spectral resolution, the type of optical filter, the stability of the optical parts and the quality of the detector. The best available detectors are of the type MCT (HgCdTe). These detectors achieve a noise level 100 times lower than those operating at room temperature.

Determination of the purity of gaseous primary reference materials

In the process of the preparation of the gas reference material, the accuracy of the gravimetric method strongly depends on the purity of the input gas used in the preparation of the calibration gas mixture. Impurities of an input gas are one of the most critical contributions to the uncertainty of the final mole fraction of the gas mixture. Contributions to the uncertainty are significantly dependent on the quantity of impurities present in the clean gas input and the accuracy with which these impurities have been measured (Bremser and Hässelbarth, 1997; Mocák *et al.*, 1996). In many cases, the purity of the gas matrix is extremely important. This is especially true when the mole fraction of the secondary component is actually very small and can be considered as an impurity in the matrix gas. It is also important to evaluate the content of additional critical impurities that can react with a minor component (e.g. oxygen present in pure nitrogen reacts with NO to give NO₂).

In the case when contamination, likely present in "clean" gas, is not detectable by the analytical method used, the molar fraction of impurities may be given as half of the detection limit of that particular analytical method.

Mole fraction uncertainty assessment is based on a rectangular distribution between 0 and the value of the analytical method detection limit. In this process, the gravimetric method

assumes that there is an equal probability that an impurity present in the "clean" source of gas may reach the value of its detection limit. Thus, the contents of undetected impurities behaving as a rectangular distribution of the standard uncertainty is defined as half of the detection limit divided by the square root of three (Rothman et al. 1998).

Detection limit and identification of gases by FT-IR

According to the accepted convention the limit of detection (LOD) is the lowest analyte concentration that is significantly different from the blank. The signal intensity (y_D) corresponding to the detection limit represents such size of the signal that is significantly different from blank value. The signal is determined by the mean value μ_B and the standard deviation σ_b of a blank signal according to the equation (Horák and Vítek, 1980)

$$y_D = \mu_b + k_D \sigma_b \quad (1)$$

where $k_D = 3$.

Because the values μ_b and σ_b are not known, their estimates are used, i.e. the average blank value \bar{y}_b and the corresponding standard deviation s_b .

Although the LOD is defined in the signal domain, the main objective in trace analysis is to obtain a concentration value of LOD, which we label the c_D . Because the values of the signal are to be corrected for the blank experiment, the corrected linear calibration dependence should theoretically pass through zero. Thus the uncorrected dependence provides on the signal axis the value of the intercept μ_b , estimated as \bar{y}_b . Then the usual method of obtaining concentration c_D is based on the use of equation:

$$c_D = (y_D - \bar{y}_b) / b_1 \quad (2)$$

If we substitute into equation (2) equation (1) given above, with the replaced values of μ_b and σ_b , we obtain for the concentration detection limit the following relationship

$$c_D = 3s_b / b_1 \quad (3)$$

where

s_b is the standard deviation

b_1 is the slope of the calibration curve, analytically identified as sensitivity.

The estimate of the standard deviation is possible by the analysis of repeated measurements of the blank experiments. This approach was adopted to evaluate the limit of detection for CO, CO₂, H₂O and propane.

A blank signal was obtained by measuring the evacuated cell down to the value of 10^{-5} mbar. The values of signal intensities (peak heights) are in the range of about 10^{-2} absorbance units. In the evaluation of the data, integrated absorbance values were used. The evaluation was carried out from five blank experiments for the individual wavelength ranges, characteristic for the absorption of molecules. These wavelength ranges have also been used for the calibration methods for each gas component.

An example shown in Figure 1 demonstrates a comparison of a blank and a sample containing carbon dioxide with concentration of 1 $\mu\text{mol/mol}$ (ppm). Both spectra were measured using the same spectral parameters (resolution 1 cm^{-1} and number of scans 30) in the wavelength range $2390\text{--}2290\text{ cm}^{-1}$. The detection limit reached was $0.13\text{ }\mu\text{mol/mol}$.

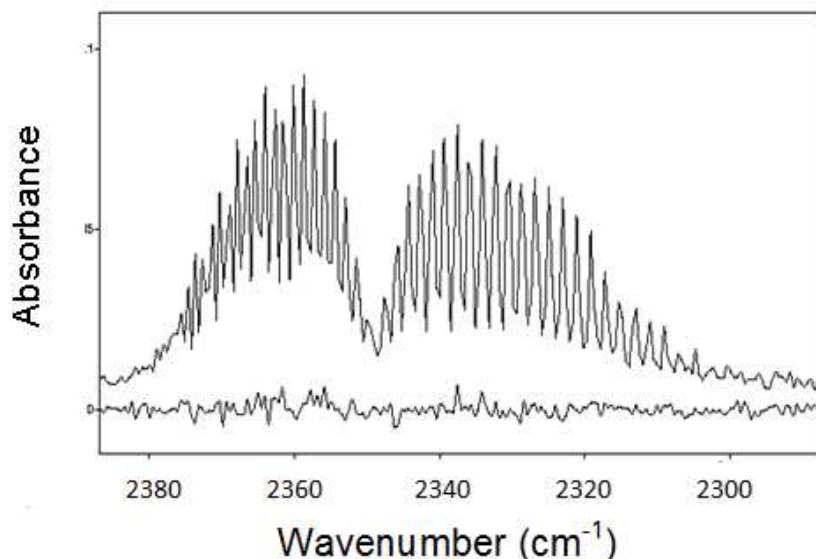


Fig. 1. Comparison of the blank (lower) spectrum with the spectrum of carbon dioxide (1 ppm).

Figure 2 shows the spectrum of super pure N₂ 6.0 used for gravimetric preparation of primary and secondary gaseous reference materials. It was found that the measured signal is reproducible within $\pm 0.5\%$ after 60 scans. Dividing the spectrum of the sample with the background spectrum, gives the absorbance spectrum shown in Figure 2. In the spectral range 2200 – 2400 cm⁻¹, absorption bands corresponding to carbon dioxide are clearly seen in Figure 2. The absorption bands corresponding to water are visible in the regions 1400 – 1600 cm⁻¹ and 3600 – 4000 cm⁻¹. Bands corresponding to carbon monoxide in the spectral region 2145 – 2155 cm⁻¹ and bands corresponding to propane in the spectral range 2911 – 3039 cm⁻¹ are very low in intensity and are almost indistinguishable from the noise. Therefore concentrations of propane and carbon monoxide were estimated from the detection limit method.

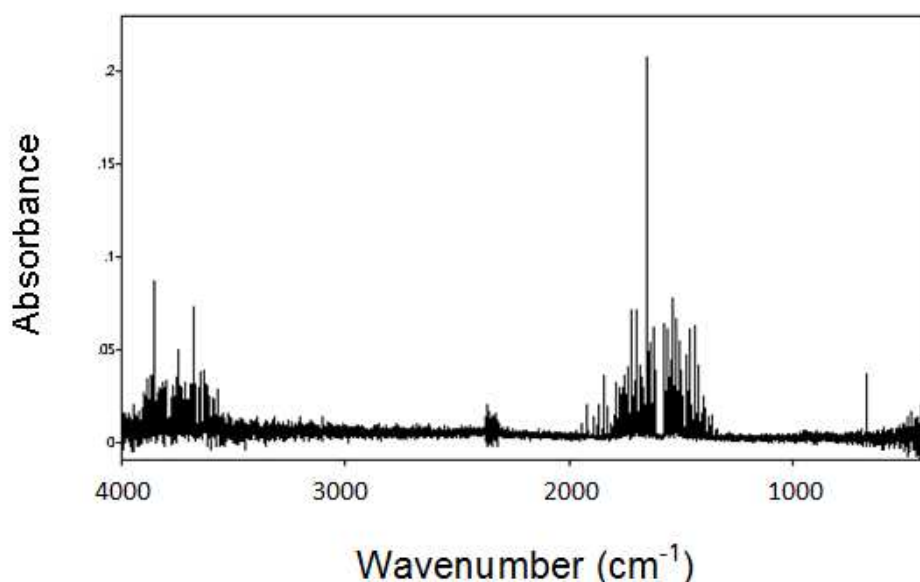


Fig. 2. The spectrum of super pure N₂ 6.0.

The absorption spectrum revealed a residual content of CO₂, CO and water. This indicates that the background spectrum and the spectrum of the sample contained different levels of water, CO₂, and CO. Our measurements showed that super pure nitrogen contained trace components CO, CO₂ and propane in the range of ± 0.1 $\mu\text{mol/mol}$. Negative values of molar fractions were also obtained, which indicate higher values of the molar fractions of these components in the background than in the sample. Trace amounts of water varied greatly, ranging from 2 -25 $\mu\text{mol/mol}$.

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