

# New applications and insights using an old technique

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**Abstract.** It has been almost 60 years since the first commercial high-resolution FTIR spectrometer was launched. In gas metrology, such FTIR spectrometers have traditionally been used for a few niche applications, but they have never become a real workhorse. The interest in FTIR has recently revived thanks to new measurement challenges involving multiple reactive gases in applications like CCUS, biogas, and hydrogen quality analysis. However, standard commercial FTIR equipment, such as the gas cell, is typically not fit for purpose for these applications. This paper will discuss some of the necessary modifications to gas cells to exploit the full potential of FTIR as a versatile tool for the selective measurement of reactive gases. Further, common pitfalls in spectral data analysis are discussed. Experimental results on reactive gases in NO<sub>2</sub> and CCUS gas standards are presented to show what can be learnt from FTIR measurements. The paper will conclude with an outlook on whether there is a future for FTIR spectrometers with the recent advent of broadband laser spectrometers with similar multicomponent measurement capabilities.

## 1 Introduction

In 1842, the Swiss physicist Jean-Daniel Colladon invented the ‘light fountain’, where light is trapped in a water jet due to total internal reflection of the light at the water-air surface. This invention was waiting a long time for a good application. Nowadays, optical fibres, based on the same principle of total internal reflection, are used to transport huge amounts of data as part of the Internet.

A somewhat similar situation occurred for the use of FTIR spectrometers in gas analysis. In the 1960s the first commercial FTIR analysers became available, and many labs active in gas analysis obtained an FTIR but typically only used it occasionally. For instance, some NMIs operate it for purity analysis of the pure gases used to make reference gas standards. However, more intensive use of the FTIR in gas analysis only occurred in the last 15 years with the emergence of new analytical challenges in applications like hydrogen quality (ISO14687) [1], Carbon Capture Utilisation and Storage (CCUS) [2] and biogas [3]. In these applications, multiple, often reactive gases need to be measured, which is ‘ideal’ for FTIR spectrometers.

This paper discusses the optimisation of the FTIR measurement cell and precautions on the use of spectral databases and, finally, shows what can be learnt from applying FTIR to the analysis of NO<sub>2</sub> gas standards and gas standards for CCUS.

## 2 Optimising FTIR cells

There are many providers of absorption cells for FTIR gas measurements. These cells can be either single-pass (providing a path length of typically 10 cm) or multi-

pass (providing a path length of typically 2.5 m up to 100 m). The single-pass cells are normally equipped with large optical windows (38 mm - 47 mm) so that they can be used with relatively large infrared beam diameters. As a result, commercial single-pass FTIR cells have a large internal surface area and volume, making them less suitable for analysis of reactive gases, in particular in static reference gas standards. At VSL we developed an optimised single-pass cell (Figure 1) for analysis of reactive gases.



Figure 1 Single-pass cells for FTIR measurements. The cell on the left is a traditional 10 cm cell, with a relatively large volume. The cell on the right has been optimised for the analysis of reactive gases by minimizing the cell volume and use of SilcoNert 2000 passivation.

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A comparison of the specifications of both cells is given in Table 1. The optimised cell has a two times longer optical path length, making it about twice as sensitive, yet with a much smaller volume and about twice the lower surface area. This results in a fast stabilisation and less use of reference gas standards. An additional benefit of the optimised cell is that the optical windows are much cheaper due to their small diameter of ½ inch.

**Table 1.** Comparison of the traditional and optimised cells shown in Figure 1.

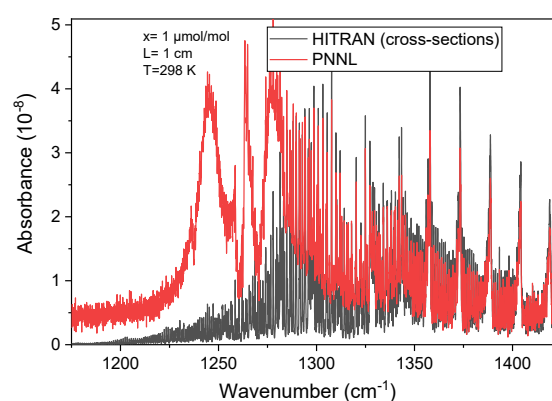
	Traditional	Optimised	<u>Traditional</u> Optimised
Volume (ml)	146	16	9.3
Surface area cell wall (cm <sup>2</sup> )	139	63	2.2
Optical path length (cm)	10.5	20.1	0.52
Passivation	No	SilcoNert 2000	

When higher sensitivity is required, multi-pass cells are used. Traditional multi-pass cells are not optimised for analysis of reactive gases or small gas samples. Only in recent years, a few manufacturers have developed optimised cells achieving a path length of 10 m with a modest cell volume of 0.5 L as compared to 2 L for traditional cells (see e.g., [4]).

### 3 Use of spectral databases

To determine the amount fraction of a certain gas in a sample by FTIR, one can use either a set of reference gas standards or rely on the use of spectral reference data. The latter option is often the only practical approach for reactive gases like nitrous acid (HNO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) for which no reference gas standards are available. For the spectral reference data of small molecules, the line strengths from databases such as HITRAN (*high-resolution transmission molecular absorption database*), GEISA (*Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information*), or EXOMOL are used. For larger molecules, absorption cross-sections are used, which can be obtained from e.g., the PNNL Quantitative Infrared Database for Gas-Phase Sensing, the NIST Quantitative Infrared Database, and HITRAN. The most widely used database is HITRAN, which contains millions of line strength data for tens of molecules and every 2 years an update appears. This compilation started more than 50 years ago, and large efforts are made to ensure that the data is reliable [5]. However, these and other spectral reference data are typically not SI-traceable. There are some efforts ongoing to increase the amount of traceable line strength data [6] and a CCQM/GAWG Task Group on Advanced Spectroscopy has recently been established to increase and coordinate this [7].

Care must therefore be taken when using spectral data from the databases. Data from different databases can differ (much) more than is expected based on the reported uncertainties of each database [8]. As an example, Figure 2 shows part of the infrared spectrum of NO<sub>2</sub> from the PNNL and HITRAN databases. There is good agreement for most wavelengths, but around 1263 cm<sup>-1</sup>, the PNNL database is too high due to the presence of an impurity, in this case HNO<sub>2</sub>. Doing such a comparison will show that there are multiple significant differences between the databases (see e.g., [9]). Therefore, users should cross-check the data from different databases before using them and, whenever possible, use reference gas standards for control and calibration.

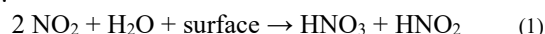


*Figure 2* NO<sub>2</sub> absorbance based on PNNL and HITRAN database. In most spectral ranges there is good agreement but around 1263 cm<sup>-1</sup> the PNNL database is too high due to the presence of an impurity (in this case HNO<sub>2</sub>).

### 4 Is HNO<sub>2</sub> present in NO<sub>2</sub> gas standards?

In the pioneering work of Fried and co-workers [10] the presence of HNO<sub>3</sub> in NO<sub>2</sub> gas standards was demonstrated using the spectroscopic methods TDLS and FTIR, as well as by using chemiluminescence in combination with a nylon filter removing all acid gases like HNO<sub>3</sub>. In 6 out of 7 cylinders, HNO<sub>3</sub> amount fractions of 2.2 to 23% relative to the NO<sub>2</sub> amount fraction were found. No HNO<sub>2</sub> was observed in these gas standards.

In literature, the formation of HNO<sub>3</sub> is typically given by:



Based on this reaction, HNO<sub>2</sub> is expected to be present at similar amount fractions as HNO<sub>3</sub>. While HNO<sub>3</sub> is consistently observed in NO<sub>2</sub> standards, HNO<sub>2</sub> has only rarely been reported in NO<sub>2</sub> gas standards [11]. Several laboratories have, in rare cases, observed HNO<sub>2</sub> but have no clear picture under which conditions HNO<sub>2</sub> is present (personal communication). In some cases, HNO<sub>2</sub> was only observed in one measurement of a mixtures but not in subsequent measurements of the

same mixtures (e.g., BIPM analysis of one of the NPL mixtures in the CCQM K74:2018).

#### 4.1 HNO<sub>2</sub> in pure NO

NO<sub>2</sub> gas standards are normally prepared starting from pure NO and not from pure NO<sub>2</sub> as the latter is only available at relatively low purity levels (~99.5%) compared to pure NO (99.99%). In high-purity nitric oxide, HNO<sub>2</sub> is observed at amount fractions of tens up to hundreds of μmol/mol (Figure 3). Other impurities that are present include N<sub>2</sub>O (increases in time in pure NO), HNO<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O.

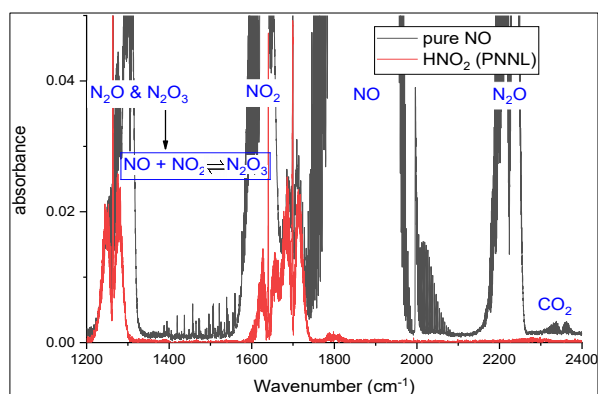


Figure 3 Measurement of pure nitric oxide showing the presence of N<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub> (exists in a dynamic equilibrium with NO and NO<sub>2</sub>), and HNO<sub>2</sub>. HNO<sub>2</sub> is typically present at around 50-300 μmol/mol in pure NO.

In diluted NO, N<sub>2</sub>O<sub>3</sub> is no longer observed, as it is proportional to the product of the NO and NO<sub>2</sub> amount fractions.

#### 4.2 HNO<sub>2</sub> absent in regular VSL NO<sub>2</sub> gas standards

In the VSL binary NO<sub>2</sub> gas standards, HNO<sub>2</sub> is not observed (Figure 4) in contrast to HNO<sub>3</sub>. The HNO<sub>3</sub> amount fraction is proportional to the amount fractions of NO<sub>2</sub> and H<sub>2</sub>O and is typically 1% relative to the NO<sub>2</sub> amount fraction.

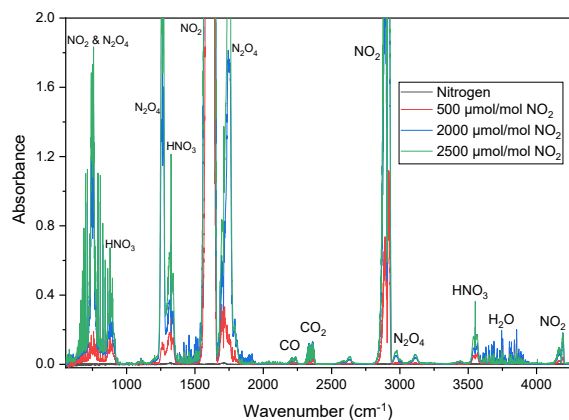


Figure 4 Measurement of high amount fraction NO<sub>2</sub> in N<sub>2</sub> standards showing the presence of the dimer (N<sub>2</sub>O<sub>4</sub>), HNO<sub>3</sub>, H<sub>2</sub>O, CO and CO<sub>2</sub>. For the 2500 μmol/mol NO<sub>2</sub> mixture, the measured N<sub>2</sub>O<sub>4</sub> amount fraction is 40 μmol/mol.

#### 4.3 HNO<sub>2</sub> in PEMS gas standards

At VSL, HNO<sub>2</sub> was consistently observed for the first time in NO<sub>2</sub> gas standards that were produced for the Portable Emission Measurement Systems (PEMS). PEMS are used to determine the emission of road vehicles under real-driving conditions [12]. These PEMS gas standards contain a mixture of NO<sub>2</sub> and NO in a matrix with percentage levels of CO and CO<sub>2</sub> in nitrogen. Figure 5 shows an example of an FTIR measurement and the comparison with the PNNL database.

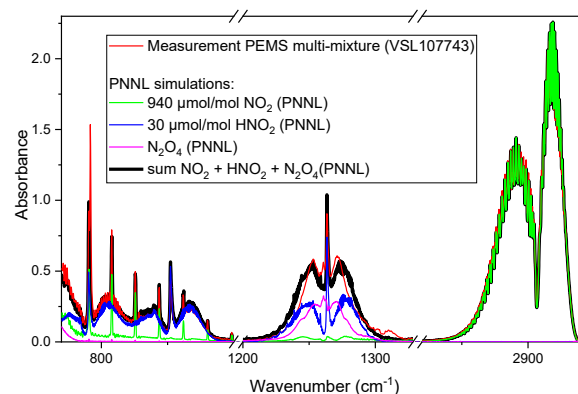


Figure 5 FTIR analysis of a PEMS multi-mixture (1001 μmol/mol NO<sub>2</sub>, 2370 μmol/mol NO, 18% CO<sub>2</sub>, 4.5 % CO in nitrogen). The picture shows 3 parts of the spectrum in which the FTIR measurement (—) is compared to a PNNL simulation (—) which is the sum of the individual NO<sub>2</sub>, HNO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> contributions.

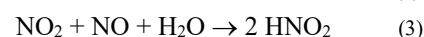
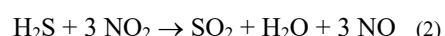
In a set of 4 analysed PEMS mixtures, all mixtures contained HNO<sub>2</sub>, while no HNO<sub>3</sub> was observed.

#### 4.4 HNO<sub>2</sub> in CCUS gas standards

For CCUS there are several standards that set limits for impurities that can be present in the CO<sub>2</sub>, as they can, for instance, have a negative impact on equipment or pipelines during transport or storage [13]. VSL prepares static reference gas standards of impurities in CO<sub>2</sub> to test and calibrate analysers for CCUS applications.

Figure 6 shows mixtures that have been prepared gravimetrically in a CO<sub>2</sub> matrix (left side) and the resulting analysis (right side). These mixtures were prepared to contain, next to NO<sub>2</sub>, two sulphur components, water, and oxygen, and the matrix gas was CO<sub>2</sub>. FTIR analysis revealed that NO<sub>2</sub> was significantly below the gravimetric amount fraction, while SO<sub>2</sub> was significantly higher. HNO<sub>2</sub> (a few percent relative to the NO<sub>2</sub> amount fraction) and NO were both formed, while HNO<sub>3</sub> was absent. Note that it is somewhat surprising that NO is present while there is also O<sub>2</sub> in these mixtures.

Possible reactions which might cause this change in amount fractions include:



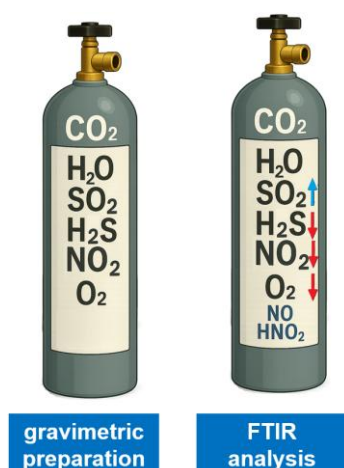


Figure 6 Gas standards with impurities at  $\mu\text{mol/mol}$  level in pure  $\text{CO}_2$  were prepared using gravimetry (left cylinder). After preparation, the impurities were measured by FTIR except for  $\text{H}_2\text{S}$  and  $\text{O}_2$  that were analysed with GC-SCD and GC-PDD. The analysis showed (right cylinder) that the  $\text{SO}_2$  amount fraction was higher than the gravimetric amount fraction, while for  $\text{H}_2\text{S}$ ,  $\text{NO}_2$  and  $\text{O}_2$  this was lower. Further, two additional components were formed in the standard:  $\text{NO}$  and  $\text{HNO}_2$ .

#### 4.5 $\text{HNO}_2$ in $\text{NO}_2$ - $\text{NO}$ gas standards

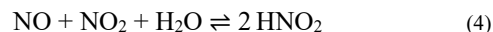
From these PEMS and CCUS examples, it could be inferred that either the presence of  $\text{CO}_2$  or the presence of  $\text{NO}$  is required for the formation of  $\text{HNO}_2$  and the absence of  $\text{HNO}_3$  in  $\text{NO}_2$  gas mixtures. To test the latter hypothesis, 3 mixtures containing only  $\text{NO}$  and  $\text{NO}_2$  in nitrogen were measured using CRDS. These measurements showed that in all 3 mixtures only  $\text{HNO}_2$  is present while  $\text{HNO}_3$  was not observed.

**Table 2.** Measured  $\text{HNO}_2$  in three mixtures (10  $\mu\text{mol/mol}$   $\text{NO} + 10 \mu\text{mol/mol}$   $\text{NO}_2$  in  $\text{N}_2$ ) of different ages.

Age mixture (years)	$\text{HNO}_2$ (relative to $\text{NO}_{2 \text{ grav}}$ )	$\text{HNO}_3$
1	1.1%	Not detected
3	1.3%	
7	1.1%	

Based on the analysis results of the PEMS, CCUS and  $\text{NO}$ - $\text{NO}_2$  mixtures, it therefore seems that  $\text{NO}$  is a prerequisite for the presence of  $\text{HNO}_2$  in  $\text{NO}_2$  gas standards. This is confirmed by FTIR measurements of 6  $\text{NO}_2$  gas standards from a specialty gas company. Some of the mixtures contained also  $\text{NO}$  and these mixtures contained then indeed  $\text{HNO}_2$  while the others did not.

A possible reaction leading to the formation of  $\text{HNO}_2$  is:



## 5 Conclusions and future outlook

The FTIR spectrometer is a solution for many of the analytical challenges for emerging applications like CCUS and hydrogen quality analysis. Using an optimised gas cell is important for correctly measuring reactive components. This paper provides the first systematic evidence that the presence of  $\text{NO}$  is a prerequisite for  $\text{HNO}_2$  formation in  $\text{NO}_2$  mixtures across multiple matrix environments.

In recent years, instruments based on mid-infrared supercontinuum lasers [14, 15] or frequency combs [16] have been developed which cover a large part of the wavelength range of a standard FTIR. Two of the main advantages of such laser-based instruments are the excellent beam quality, allowing the use of even more compact measurements cells (or even cavity enhancement to obtain kilometre long path lengths and down to 1 pmol/mol sensitivity for many molecules [17]!), and the high repetition rate, enabling fast measurements. In the next decade, such systems may take over the new role FTIR has just acquired in gas analysis.

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