ONLINE GAS CHARACTERIZATION BY ADVANCED SPECTROMETRY

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ABSTRACT

Online characterization of off-gas by spectroscopic methods is well established and commercial instrumentation is available for monitoring. Normally, these instruments operate at gas temperatures at or below 200 °C and are well suited for end-of-pipe emission monitoring. Even when monitoring gas constituents that are stable at the sampling temperature, a change in chemical equilibrium might alter the gas composition from that of the actual gas temperature. An increase of the sampling temperature is limited by increased interference from emission when using absorption spectroscopy as analytical method. At higher temperatures emission spectroscopy can be applied with minimal interference from absorption. However, commercial instrumentations based on emission spectroscopy are very scarce since optical access is process specific. In many metallurgical processes, it is of paramount importance to know the exact gas composition in the reaction zone. For emission spectroscopy, the primary challenge is to facilitate collection of emission from the reaction zone. It is challenging to gain optical access to the reaction zone without introducing some temperature gradients. Also, materials transparent to the wavelengths used must also be thermally stable at these elevated temperatures. In this paper, we present some of the approaches to these challenges currently being investigated at SINTEF. We present results showing that emission spectroscopy is well-established as a quantitative methodology for gas monitoring using in-house spectroscopic hardware. We also demonstrate some approaches to gaining optical access to the reaction zone, including use of optical fibers. Finally, examples from monitoring of low concentration greenhouse gas emission by use of Fourier transform infrared spectroscopy with improved sensitivity are given.

KEYWORDS: *Spectrometry, Fourier-transform infrared spectroscopy, emission spectroscopy.*

1. INTRODUCTION

Online characterization of stack and fugitive gas emissions has been realized through the development of transportable, analytical instrumentation with adequate sensitivity. Although conventional sampling still benefits from the possibility of pre-concentration of analytes, the benefits from online monitoring of gas emissions are abundant. In the case of labile and sticky gas constituents, online characterization is a requirement. Another emerging field of the interest is the ability to dynamically qualitate and quantitate the gas compositition in order to, through the knowledge of reaction intermediates, improve the understanding of the reaction processes. During the last four years, SINTEF has conducted several measurement campaigns in order to evaluate the performance and applicability of new spectroscopic instrumentation. Some of these results are explored in this paper.

2. OPEN-PATH FOURIER TRANSFORM INFRARED SPECTROSCOPY

OP-FTIR spectroscopy makes use of an open path where the light is reflected back to the

detector by means of a collimating mirror. According to Beer's law, the absorbance is proportional to the light path and this parameter can thus be utilized for improved analytical sensitivity. The signal to noise ratio, however, deteriorates with path length as transmission of light is reduced. Strong light absorbers (ie. particles, water vapor and carbon dioxide) in the path also limit the maximum path length that can be utilized. Calibration of OP-FTIR instrumentation can be performed by making use of a short, closed measurement cell, inserted between instrument and mirror, where the gas composition can be controlled. Once a calibration model is established, typically through multivariate regression, the model can be applied to estimate the average gas composition in the light path.

An early application of SINTEF's ABB MR170SC spectrometer was to evaluate the ammonia concentration over a settling tower at a ferroalloy smelter. Setting up a light path across the diameter of the tower proved impossible as the light transmission at 2600 cm^{-1} was too low. Visually, the water vapor was so dense that the mirror could not be seen across the diameter. By setting up a 5.7 m (total path of 11.4 m) secant path, sufficient transmission was secured. The ammonia concentration was found to be in the range 5-10 ppmv, which was verified by two online extractive FTIR spectrometers. Although the average estimate as adequate, large variation in the estimate was seen from the effect of the water vapor in the path. In the case of ammonia, extractive FTIR was shown to have better analytical performance. In the case of sticky or labile gas species, OP-FTIR would be the better choice in strategy.

Another OP-FTIR application within ferroalloy production has been to evaluate the gas composition over the slag pit when sprinkled with water. Periodical foul stench motivated the search for sulfur compounds. The instrumental installation is shown in figure 1 (left). A background spectrum was recorded when water was not sprinkled over the pit. The absorbance of gases measured during sprinkling could then be found from the logarithmic ratio of the background and the recorded spectra. The temperature of the gas changed significantly between sprinkling and not, and this was seen to affect the recorded spectra. The entire intensity of spectra changed with time, introducing large variance in the calculated absorbances. With the long path applied (49.2 m), the spectra were saturated in the range 1400-2000 cm^{-1} and 2200-2400 cm^{-1} from water and carbon dioxide respectively. Nevertheless, qualitatively the spectra could be used to evaluate for constituents in the gas. Sulfur dioxide and carbon monoxide were clearly present, and the concentrations were estimated to be maximum 12.5 and 5.2 ppmv, respectively. No trace of sulfur trioxide was observed although a shoulder to the sulfur dioxide peak gave indication of a sulfur containing constituent.

A similar configuration was used for a 15.6 m path setup across the tapping area. Again, water and carbon monoxide saturates the spectra in their dominant rages, and mask possible detection of COS, CS_2 and H_2S. Sulfur dioxide and carbon monoxide concentrations were estimated to be maximum 13 and 2 ppmv. No indication of phosphine, arsine or silane was found in the recorded sprectra; the spectra had scope to detect these species down to the 1 ppmv level.

A more convincing application of OP-FTIR has been demonstration in aluminum primary production. Due to the high concentration of HF in the raw gas, direct application of extractive FTIR spectroscopy is damaging to the spectrometers. Therefore, HF filtering has to be employed [1]. Filtering also removes other gas constituents of interest. In Aluminum primary production, the formation of PerFluoroCarbon (PFC) gases is of interest. Although emissions are low, these components have Global Warming Potentials (GWP) up to 10,000 higher than carbon dioxide. The mechanism of formation for PFC is still debated; a possible intermediate COF_2 would allow for lower formation potentials than the case for CF_4 [2]. COF_2 decomposes readily in the presence of water, forming CO_2 and HF, and cannot be measured by extractive FTIR spectroscopy. Another labile compound of interest was SO_3.

Figure 1: OP-FTIR application over slag pit (left) and during tapping (right)

The same ABB OP-FTIR spectrometer was used to beam across a ~300 kA electrolysis cell. The path was set above the alumina feeding holes. As the opening at one end of the cell was only 30 cm high, the beam has an elevation profile from 30 cm on one side to about 130 cm on the opposite side. The setup is shown in figure 2.

Initial readings indicated that continuous cell feeding was introducing high variation in transmittance. Feeding was stopped and this resulted in by far more stable transmittance, as well as reduced emission from dust. Through underfeeding of alumina to the process, the cryolite electrolyte is discharged as a result of elevated anode potentials, eventually resulting in the formation of PFC gases. The concentration profiles of relevant gas species is shown in figure 3.

This is the only evidence of COF_2 formation in an industrial scale electrolysis cell known to the authors. As seen from figure 3, its concentration profile is fairly similar to that of C_2F_6, with a peak concentration of approx. 15 ppmv. An individual absorbance spectrum is shown in figure 4 to justify the presence of COF_2 in the path.

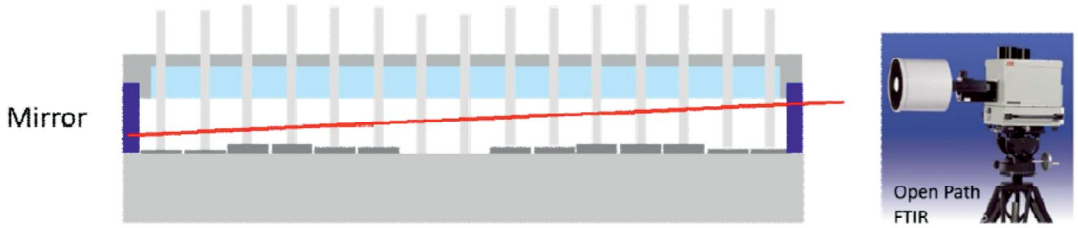


Figure 2: OP-FTIR configuration through an aluminum electrolysis cell

As seen in figure 4, the spectral range 12-1300 cm^{-1} contains absorption bands by CF_4, C_2F_6 as well as COF_2. C_2F_6 was quantified from its peak at 1120 cm^{-1}, while the only peak of CF_4 at 1280 cm^{-1} was used. For both peaks the signal was close to saturation. Added the effect of emission from dust made quantification of both species very difficult. The estimated peak concentration of COF_2 (estimated from 950 cm^{-1}), although subject to high degree of uncertainty, was estimated to be 15 ppmv. All spectra were scanned for C_3F_8 but this proposed PFC species was not detected during this experiment. Relevant for sulfuric acid dew point assessment, spectra were also scanned for SO_3 and H_2SO_4. Neither of these could be detected.

Another successful application of OP-FTIR is the monitoring of fugitive emissions in aluminum primary production. As the combined dry and wet scrubbing of off gases for HF and SO_2 is highly efficient, the fugitive emissions are highly significant. For the PFC and COS passing readily through the scrubbers, the fugitive emissions are less significant.

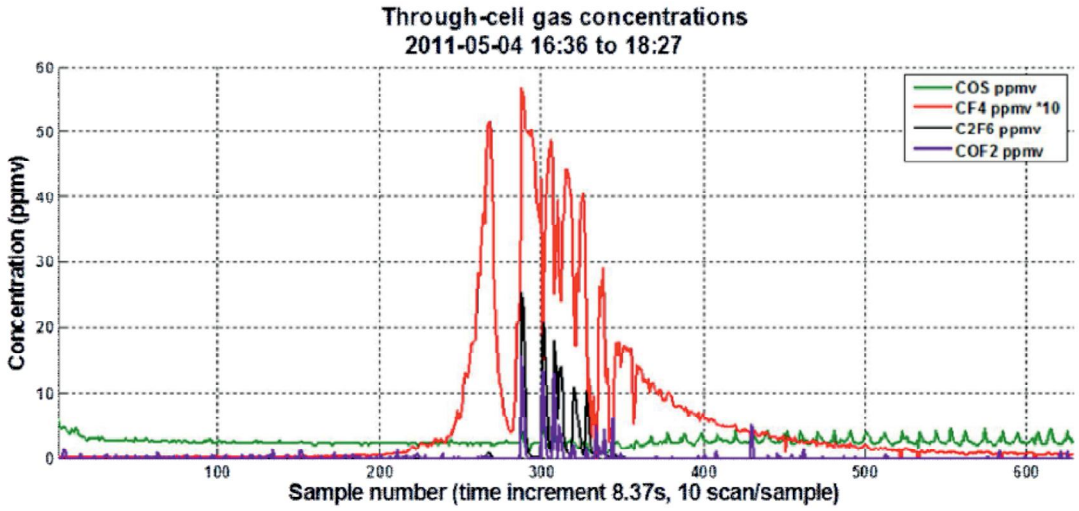


Figure 3: Concentration profiles for selected gas components through the anode effect. The sawtooth concentration profile shapes stems from the turbulence of the anode effect as well as the fact that the alumina feeding was initiated to cure the anode effect

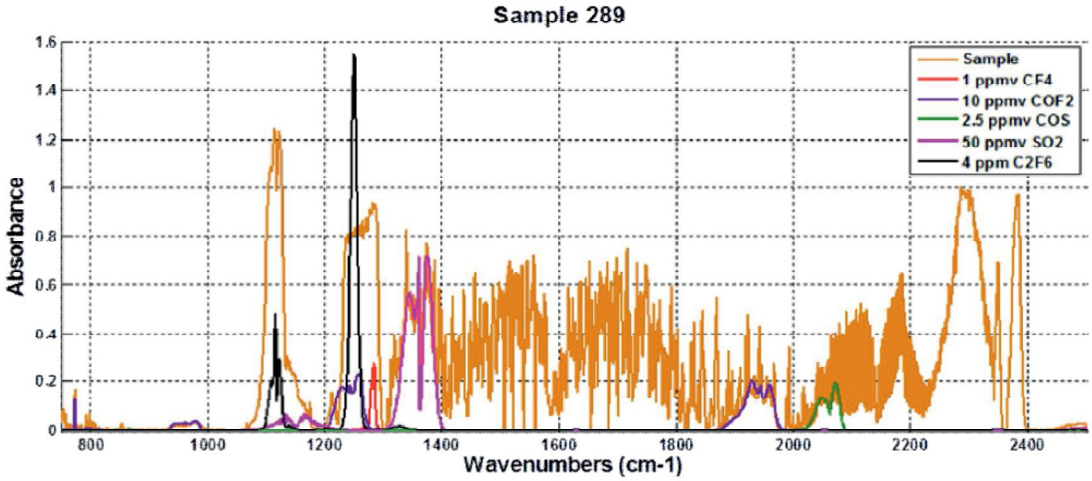


Figure 4: Individual absorbance spectrum during anode effect overlaid selected reference spectra of relevant gas compounds

The instrument was setup on the roof of a smelter with a total path length of 46 m as shown in figure 5. Out of curiosity, tracer SF_6 gas was released for evaluation of gas dilution at the closest electrolysis cell, followed by the initiation of an anode effect on the same cell.

The maximum concentration of CF_4 was estimated to be 450 ppb ± 25%. The limit of detection was estimated to be 10 ppbv. Fugitive emissions of C_2F_6 could not be detected. For HF and SO_2 the averaged concentration over approx. 1.5 hours was found to be 1.3 ± 0.2 ppmv and and 122 ± 20 ppbv respectively. Located near the light path was a manual sampling point for HF and SO_2. Obtaining data from the smelter laboratory for the three day sampling interval of which we were present revealed a fairly good correlation: the reported estimates were 0.5 ppmv and 122 ppbv respectively.

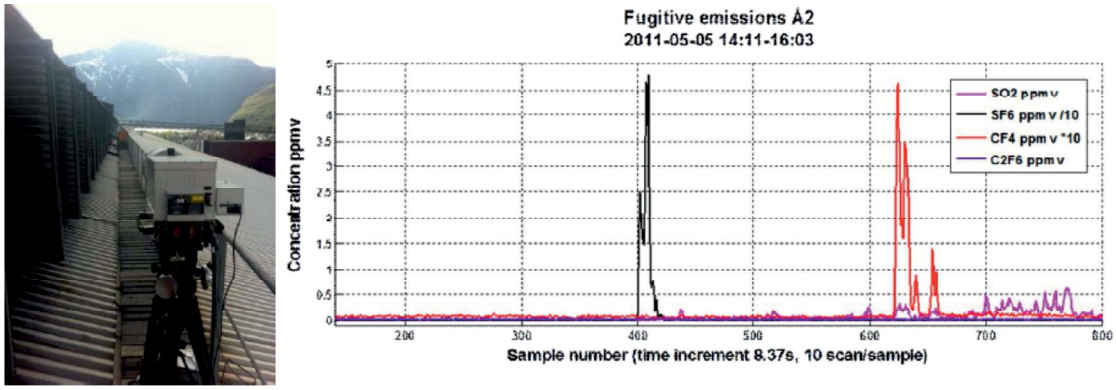


Figure 5: OP-FTIR setup for fugitive emissions (left) and concentration profiles for PFC, tracer gas and SO_2 (right)

3. EMISSION SPECTROSCOPY

Infrared absorption spectroscopy is based on characteristic molecular absorption resulting in a vibrational spectrum. Extractive sampling of gas is often limited to 200°C. At higher temperatures, thermal excitation of molecules above the ground state occurs. Relaxation of these molecules causes emission at the same wavenumbers thus resulting in a mixed spectrum that cannot be easily applied for qualitative nor quantitative purposes. Omitting an IR light source and considering the hot gas a source of emission, IR spectra can be recorded and analyzed by a conventional FTIR spectrometer.

Whereas there for conventional FTIR spectroscopy is abundant conventional instrumentation available, this is not the case for emission spectroscopy. The main reason is that the optical access to the radiation is not easily standardized, and must be adapted for the application. There is an inherent challenge with thermal blackbody radiation from the spectrometer itself in addition to that of the furnace or gas confinement of elevated temperature. The blackbody radiation is a continuum contributing to noise only. In order to minimize noise, field-of-view has to be limited by cold apertures and using a cold background in the gas confinement in the field-of-view. Emission spectroscopy can also make use of the UV-VIS spectral range. Although electronic transitions are less informative for gas molecules, spectral information from electronic transitions associated with a free electron pair of intermediate gas radicals can be utilized.

SINTEF has evaluated the use of emission spectroscopy in a silicon smelter in Norway. By installation of a IR spectrometer across an off-gas channel and with a cooled background opposite within field-of-view, several applications were evaluated. Firstly, temperature was evaluated by using the saturated part of the CO_2 spectrum and calculating temperature from Planck's law. Verification measurement performed were in excellent agreement with the spectroscopic measurements. Similarly, good estimates of the water and CO_2 concentration in the gas could be obtained. For the dust content in the gas consisting mainly of SiO_2, a fair correlation was found. Some problems with saturation were faced, although optimization of the dust estimates could be performed. An attempt to estimate the total carbon content of the gas showed poor correlation. Some of the challenges were ascribed to the fact that the model for total carbon did not take free carbon and SiC into account.

More fundamentally, there is currently a lot of activity on the use of natural gas as a source of carbon for the reduction of metal oxides. Experiments are mainly conducted on the laboratory scale. Off-gases (CO, CO_2, H_2, CH_4 and water) give important information about the reduction processes. The fact that significant amounts of methane cracks into hydrogen and carbon already at 1000°C makes it difficult to provide sufficient energy to the reduction process without experiencing loss of methane to cracking. One way to mitigate cracking is to add hydrogen to the feed gas, shifting the

cracking reaction to the left. Although cracking of methane is not desirable, the dehydrogenation of methane is required in order to utilize its carbon as a reducing agent. Ostrovski [3] proposed the following scheme:

$$CH_4(g) = CH_4(ad)$$

$$CH_4(ad) = CH_3(ad) + H(ad)$$

$$CH_3(ad) = CH_2(ad) + H(ad)$$

$$CH_2(ad) = CH\ (ad) + H(ad)$$

$$CH(ad) = C(ad) + H(ad)$$

It is therefore of paramount importance to understand the mechanisms of these two reactions competing for the fate of carbon. One approach to this is to make use of *in-situ* emission spectroscopy in order to be able to estimate the actual gas composition at the reaction temperature. The main challenge with this approach is to gain optical access to the reaction zone in a high-temperature furnace. The most common approach is to make direct optical access through IR and/or UV-VIS transparent windows. Another approach is to use optical fibers. By applying fibers of temperature tolerant material (ie. sapphire or graphite), high temperatures can be tolerated.

SINTEF has already experience from monitoring of methane concentration in a flow cell by means of InfraRed Emission Spectroscopy (IRES) [4]. The experimental setup is shown in figure 6.

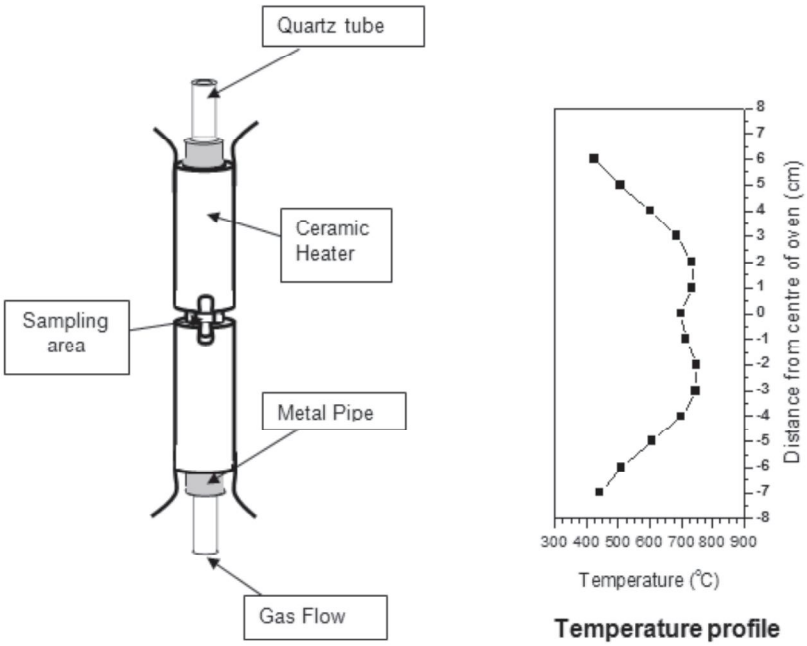


Figure 6: Left: schematic drawing of the in IR emission cell (front view). Right: temperature profile measured inside the quartz tube (oven temperature = 700°C; 5 ml/min N_2 flow)

Key to success is the design of the gas cell with optical access. The emission spectra for

methane and the relevant emission from background are seen in figure 7.

In this case, because of the relatively fair transmission through quartz around 3000 cm-1, the background emission is shown to have low impact on the emission signal from methane. Quantitation was attempted at three temperature levels for various concentrations of methane in the cell. The results are shown in figure 8.

Clearly, the quantitation show excellent performance down to the 5000 ppm level.

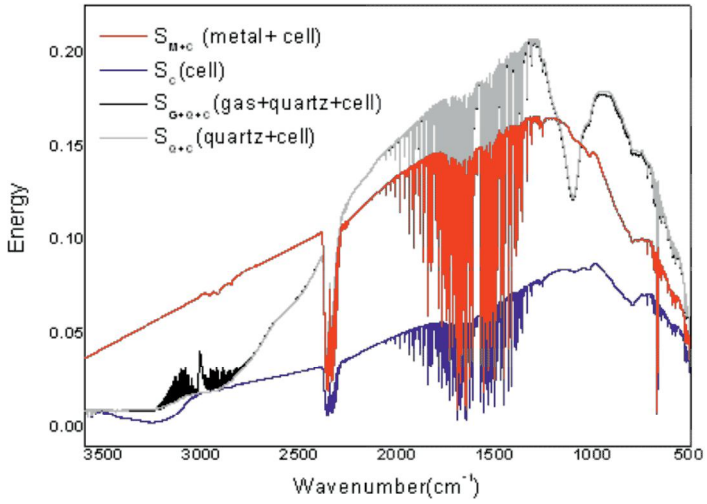


Figure 7: Single beam spectra recorded for different components of the experimental set up: S_{G+Q+C} = gas + quartz tube + cell spectrum (black line), S_{Q+C} = quartz tube + cell spectrum → *background* (gray line), S_{M+C} = metal rod + cell spectrum (red line), S_C = cell spectrum = heaters + metal pipe (blue line)

4. LONG-PATH FTIR SPECTROSCOPY

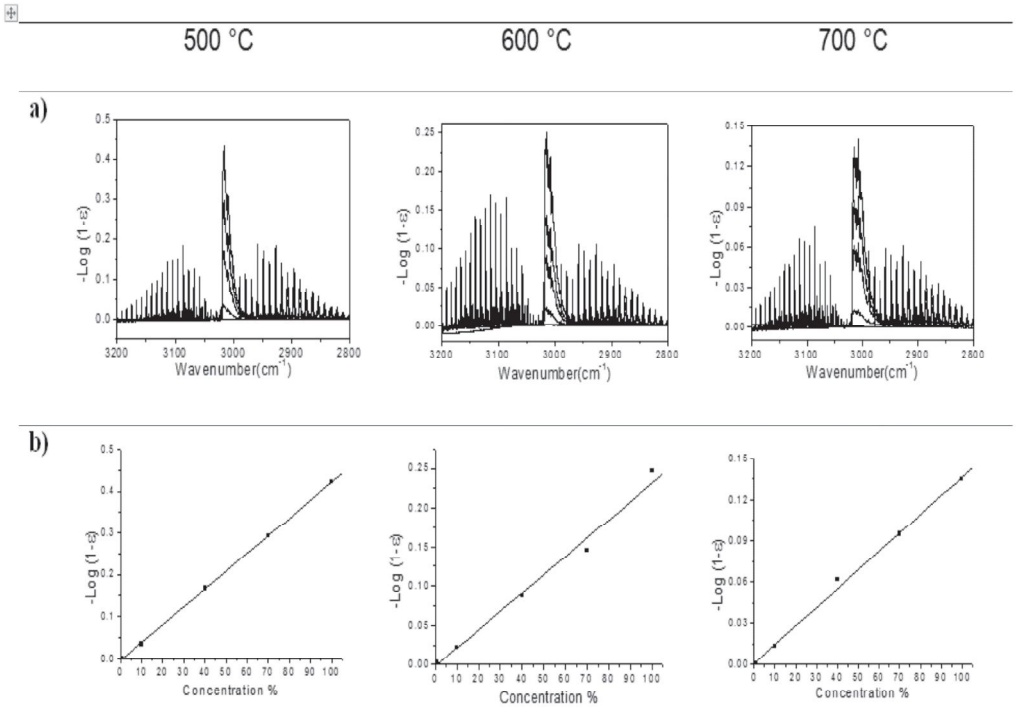
In the case where extreme sensitivity during online analysis is required, Beer's Law suggests manipulation of the light path length. In a closed cell, light can be reflected several times. SINTEF has acquired a 30 m cell of low volume (8 L) where pressure and temperature can be manipulated.

In the case of PFC GHG gas monitoring, very high sensitivity is required to monitor so-called continuous emission from trains of more than 100 electrolysis cells. SINTEF therefore wanted to investigate the best possible performance for FTIR when it comes to CF_4. Instrument setup and spectra is shown in figure 9.

For the DTGS detector, the estimated limit of detection was better than 1 ppbv. With the application of a MCT detector, a tenfold improvement in detection is expected.

5. CONCLUDING REMARKS

The potential of spectroscopy and particularly emission spectroscopy at high temperatures has proven to be a valuable tool for monitoring of emissions. Further, availability of high resolution spectra allows for convenient identification of unknown, harmful and environmentally adverse compounds. The technologies described here are partly at their infancy and will require some research efforts before the methods are applicable easily or instruments are available of the shelf.



a) IRES spectra of methane on a $-\log(1-\varepsilon)$ scale at various dilutions in Ar and different temperatures (500, 600 and 700°C) obtained by applying eq. 4 and eq. 5.
b) Plots of the $-\log(1-\varepsilon)$ peak intensities for the C-H stretching band at 3019 cm^{-1} as a function of methane concentration (100%, 70%, 40%, 10%, 1%, and 0.5%v/v); the reported line is the best fit to the data

Figure 8

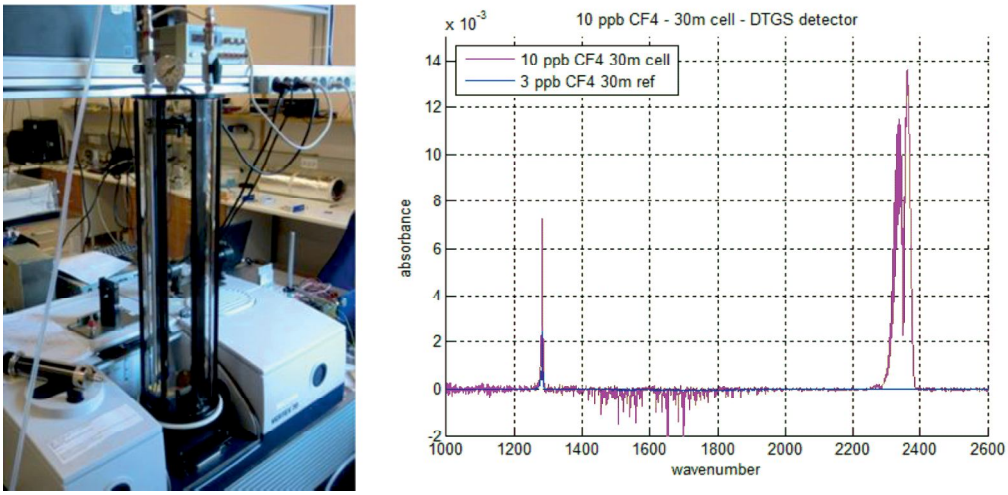


Figure 9: Left: Bruker Vertex 70 with InfraRed Analysis 35 m path mounted. Right: 10 ppbv CF_4 spectrum (magenta) overlaid 3 ppbv CF_4 reference spectrum

6. ACKNOWLEDGEMENT

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