

Validation of Online Monitoring of PFC by QCL with FTIR Spectroscopy

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Abstract

Monitoring of perfluorocarbon (PFC) evolution from aluminium smelting is gaining attention, not only because of their high greenhouse gas potentials but also due to process optimization purposes. Conventionally, PFC monitoring has been conducted by extractive sampling and subsequent analysis by fourier transform infrared (FTIR) spectroscopy. With FTIR, the quantification can be performed by IR spectral features specific for PFC. The downside is a requirement of gas scrubbing to remove HF detrimental to the instrument as well as relatively poor gas dynamics due to the large internal gas volume of the instrument. With emerging quantum cascade laser (QCL) technology, online monitoring can now be conducted with duct mounted lasers with calcium fluoride optical windows. However, due to a strong spectral overlap of CF₄ and other gas constituents present in the process (e.g. methane), the QCL instruments currently suffer from some cross-interference. In this work, QCL single cell PFC monitoring has been validated by simultaneous monitoring with FTIR.

Keywords: PFC monitoring, FTIR spectroscopy, Greenhouse gas emission

Introduction

PFC are highly potent greenhouse gases with long lifetimes, and primary aluminium production has been identified as one of the largest anthropogenic sources [1]. The theoretic fundament for the formation of the most common species, tetrafluoromethane and hexafluoroethane has been described in numerous papers [2-5]. PFC formation was initially assumed to be formed during discrete cell voltage excursions, typically in the range of 6-8 volts. Guidelines for the establishment of PFC emission inventories aim to develop correlations between smelter specific PFC emissions and production parameters (production, anode effect duration or overvoltage)[6, 7].

More recent monitoring of PFC emissions has shown that the evolution of these greenhouse gases is not confined to what been defined as anode effects [3, 8-10]. Whereas the CF₄ concentration emitted from these low voltage anode effects are low, their duration is higher. Reports from China suggest that these emissions contribute significantly to the overall inventory [11-13].

FTIR spectroscopy has traditionally been one of the preferred techniques for PFC assessment. In addition to critical compactivity of features like portability and tolerance for magnetic fields, FTIR spectroscopy benefits from multivariate calibration which enables better tolerance towards interference as well as error estimation [14]. Sufficient sensitivity for CF₄ is normally adjusted with the gas cell path length. By application of long path lengths, there is a penalty on the gas dynamics [3]. With sufficient resolution, interference from water lines on CF₄ can significantly improve sensitivity. While the cost of FTIR spectrometers has been somewhat reduced, FTIR instruments are still quite expensive and require high-maintenance [15]. Online monitoring of PFC evolutions has therefore been scarce.

The reason why laser monitoring systems do exist for HF and SO₂ commercially but not for PFC is the lack of a viable light source in the mid-infrared range. With the advent of QCL technology, mass production will eventually render the cost competitive for commercialization into PFC continuous emission monitors (CEM) [16]. The required instrument sensitivity for CEM technology is assumed to be in the range of 1-10 ppbv when applied to the gas treatment center exit ducts. These ducts are typically in the range of 2-6 m [15].

In this work, a prototype of a QCL-based in-situ CF₄ monitor[17] was installed on the duct of a single aluminium electrolysis cell in order to provide continuous concentration measurements of CF₄ evolution from the cell. For a period of three days, the QCL concentration measurements were compared with the concentration estimates of two FTIR spectrometers. One of the objectives was to observe the influence of the interference of water and methane on the single wavenumber QCL, and compare it with the FTIRs where the interferences could be removed either by gas scrubbing (water) or by use of alternate wavenumbers.

Experimental

The LaserGas™ prototype (QCL was installed by flanges on the duct of a single electrolysis cell. The light path was 0.4 m. Temperature and pressure were initially measured, and these values set in the QCL configuration software. The QCL was configured to provide a concentration estimate every 5 s. The QCL was calibrated in the laboratory using a 4.65 ppmv ($\pm 5\%$) certified CF₄ calibration standard applied to a 735 mm gas cell. The measurement range of the prototype is specified to be 0-4000 ppb m with a detection limit of better than 20 ppb m. That means, during the installation with an optical path length of 0.4 m, the detection limit was 50 ppb.

A Protea ProtIR 204M (1 cm⁻¹ resolution, 6.4 m path, 2.7 L cell volume, stirling-cooled MCT detector) was connected to the duct by means of a 20 m heated (180 °C) sample line. Water and HF were scrubbed from the extracted gas by means of two 500 mL columns filled with Drierite® and activated alumina respectively. The instrument gas cell was heated to 180 °C. Gas extraction was performed by a membrane pump, with an estimated flow rate of about 2.5 NLpm. The instrument was set produce results from three single spectra as to provide optimal dynamics.

For quantitation of CF₄, the ProtIR instrument made use of a partial least squares (PLS) calibration model. For concentrations below 45 ppmv, a spectral range between 1200 and 1313 cm⁻¹ was used. The calibration model was built from 120 spectra with 5 principal components. In order to avoid saturation of absorbance at higher concentrations, the manufacturer's PAS software logic switches to spectral ranges 1200-1259, 2165-2200 and 2464-2622 cm⁻¹ for concentrations above 45 ppmv. For the high concentration range, the PLS model was built from 125 spectra and using 7 principal components. The model was built for a concentration range up to 150 ppmv.

As the estimated detection limit of the ProtIR was 30 ppbv, an additional FTIR instrument was added to the sample line. This Bomem MB154 spectrometer with a LN₂ cooled MCT detector was initially equipped with a 35 m, 11 L gas cell for optimal sensitivity. Due to large penalty on gas dynamics, alternatively an 8 m cell with 0.8 L volume was used. When studying the dynamics of the instruments, the order to the instruments was switched in order to find the T₉₀ response of the first instrument. For the Bomem instrument, quantitation of CF₄ was performed manually by linear regression of absorbances from calibration spectra.

Calibration of the FTIR instruments was performed periodically by using a 5 ppmv ($\pm 2\%$) CF₄ standard connected to the probe end of the sample line. Eight calibrations were conducted throughout the three-day sampling period.

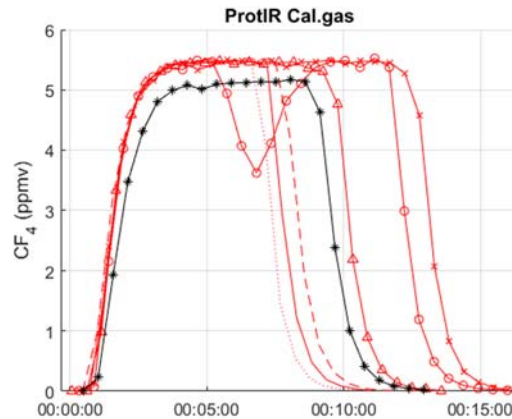
Results and Discussions

FTIR calibration and response time calculations

When comparing FTIR instruments with extractive sampling with a duct-mounted QCL with a response time lower than 5 s, it is important to know the dynamics of the extractive sampling. Calibration and T_{90} response data is summarized in Table 1. The ProtIR was generally over-estimating by 10 % for the first calibration gas bottle assuming true value to be 5 ppmv. The T_{90} response time was around 2.5 min. The Bomem instrument had a slightly lower concentration estimate than that of the ProtIR. With the 35 m cell, the response time was generally higher than four minutes. With the 8 m cell, the response time was down to 100 s.

Table 1. Calibration and T_{90} response times for FTIR instruments. For the calibration run number 8, a new 5 ppmv CF_4 bottle was used.

Cal Run	ProtIR		Bomem		Comment
	CF_4 (ppmv)	Response Time T_{90} (min)	CF_4 (ppmv)	Response Time T_{90} (min)	
1	5.46	2:33			ProtIR
2	5.48	2:31	4.99	4:21	ProtIR -> Bomem (35 m)
3	5.43	2:38	5.22	3:49	ProtIR -> Bomem (35 m)
4	5.39	2:28			ProtIR
5	5.44	2:35	5.10	4:30	ProtIR -> Bomem (35 m)
6	5.45	2:32	5.21	4:19	ProtIR -> Bomem (35 m)
7	5.44	2:32	5.18	2:44	ProtIR -> Bomem (8 m)
8	5.11	2:58	5.09	01:40	Bomem (8 m) -> ProtIR



The calibration plots are summarized in

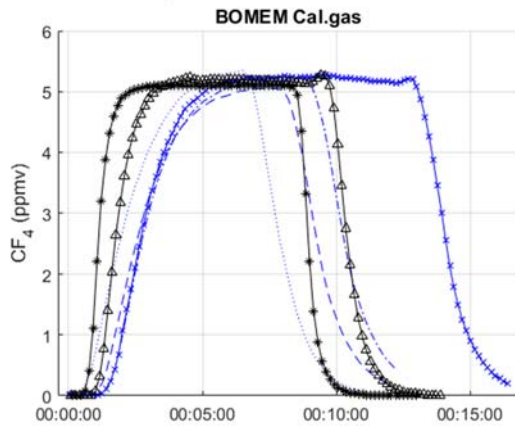


Figure 1:

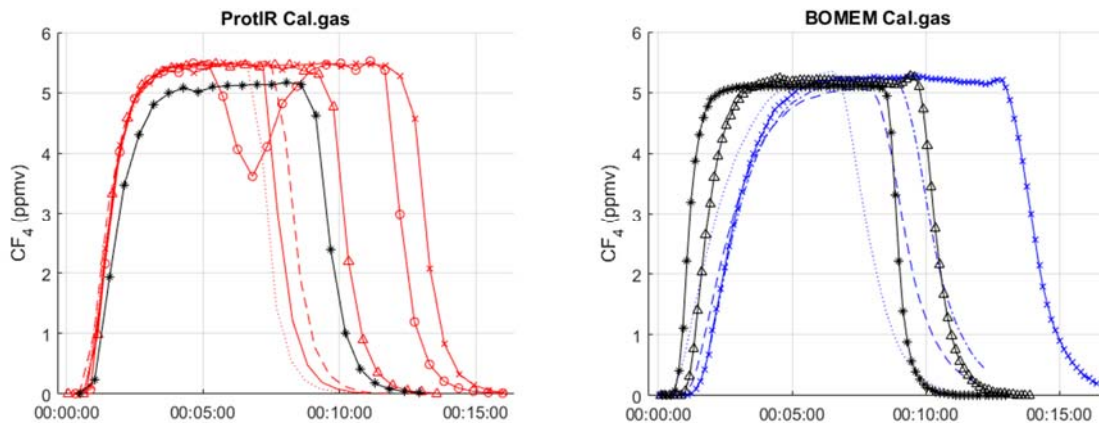


Figure 1. Left: Red lines represent the ProtIR instrument responses to calibration gas. The black line with asterisk in the graph on the left represent the ProtIR response when installed after the Bomem cell with 8 m path length (reduced CF_4 max. concentration due to use of two different batches of calibration gases with 5 ppmv ($\pm 2\%$) CF_4). Right: The blue lines represent the Bomem instrument responses with 35 m path length (11 L). The black line with upward-pointing triangles shows the response of the Bomem cell with 8 m path length (0.25 L) installed after the ProtIR, while the black line with asterisks represents the response of the Bomem cell with 8 m path length (0.25 L) when it is installed in front of the ProtIR.

Estimation of detection limits

The detection limits for the FTIR instruments were calculated from the IUPAC definition of having a signal to noise level of more than three standard deviations [18]. The estimates are shown in Table 2.

Table 2. Estimation of detection limit (LOD).

Instrument	Cell length (m)	LOD CF ₄ (ppbv)	LOD C ₂ F ₆ (ppbv)
ProtIR 204	6.4	30	30
Bomem MB 154	35	2	5
	8	5	12

For the Bomem instrument, the improvement of LOD from 5 to 2 ppbv by shifting from a 0.25 L gas cell to one of 11 L imposes a severe penalty on the dynamics. For this application, the sensitivity was the primary objective of the Bomem instrument, ensuring that the continuous PFC emissions could be monitored at the lowest possible levels.

Comparison between FTIR and QCL

The objective of the comparison was to evaluate the performance of the QCL CF₄ quantitation at low concentration levels. The time interval in Figure 2 is plotted to illustrate the importance of external calibration. As seen from the data when plotting a smoothed (N = 100) line it appears to be a CF₄ peak at around 18:50. While the peak maximum is 15 ppbv, the background signal is at -10 ppbv indicating that the QCL is operated below its detection limit. This makes it impossible to integrate CF₄ emissions over time. It should be noted that a possible source of concentration estimate offset for the QCL is the fact that the temperature and pressure values were fixed in the instrument rather than being fed to the instrument dynamically from transducers.

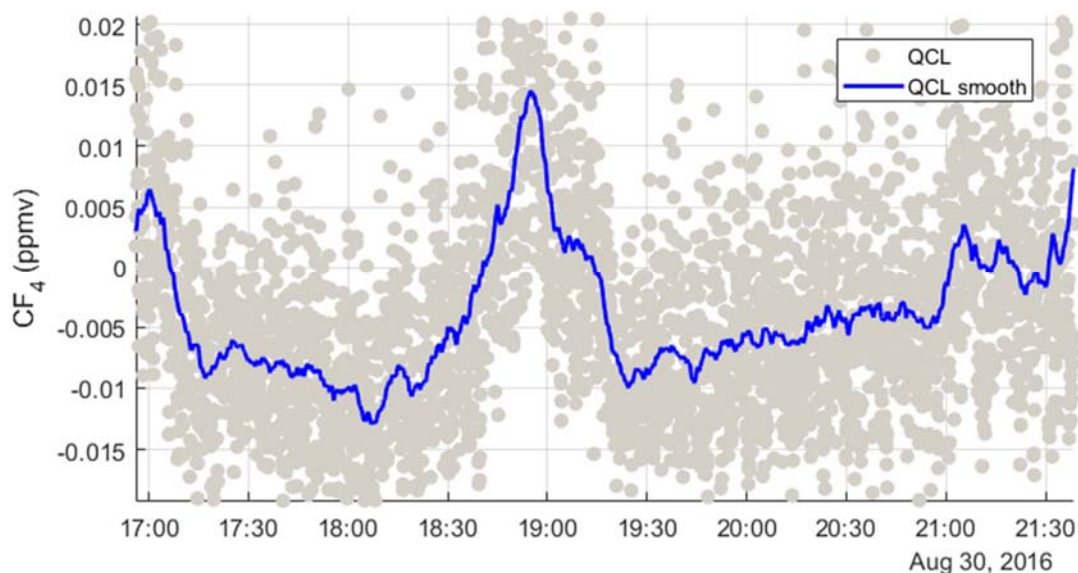


Figure 2. QCL response during a time interval where both FTIR's were offline.

To illustrate the difference in sensitivity between the FTIR instruments, a time segment is plotted in Figure 3. The ProtIR calibration model is reporting noise below the estimated detection limit at 30

ppbv. The three major peaks are clearly distinguishable on both instruments. The significance of minor peaks found at 13:00 and 14:15 would be hard to evaluate without the Bomem instrument.

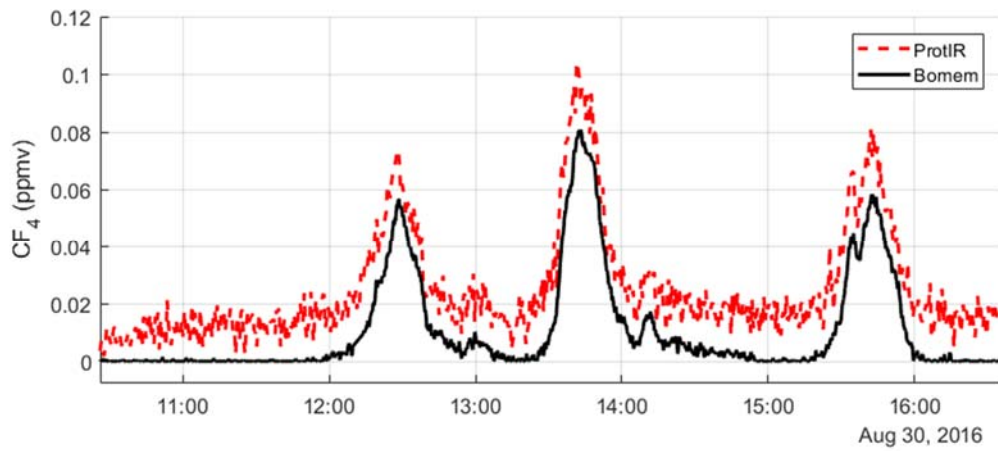


Figure 3. ProtIR (6.4 m) and Bomem (35 m) response to CF₄.

Figure 4 compares a time interval where CF₄ concentration estimates are provided from three instruments during events of low voltage CF₄ emission. Whereas the FTIR estimates are more in agreement that what was observed in Figure 3, they still show a clear difference from the QCL. At 10:30, the FTIR estimates are in the range of 5 ppbv whereas the QCL is reporting around 50 ppbv. It is also apparent that while the dynamic behavior of the QCL is superior, the concentration estimates after the two peaks appear to flatten out at around 50 ppbv. This response from the QCL is below its detection limit and should therefore not be considered significant.

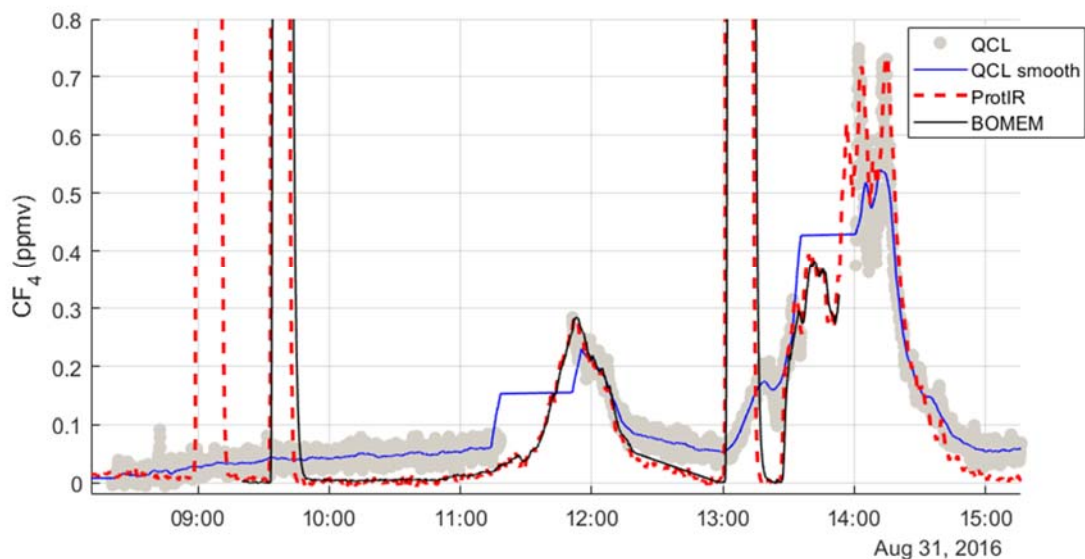


Figure 4. Comparison of concentration estimates from QCL and FTIR's during low voltage anode effects. Three calibration sequences with concentration excursions to 5 ppmv was performed during the time interval.

The QCL was not configured for monitoring of full anode effects at single cells, with a maximum range of 10 ppmv at 0.4 m path length. As shown in the inset of Figure 5, the peak value of the QCL was 61 ppmv whereas the ProtIR estimate was 343 ppmv. As the ProtIR calibration was based on spectral data up to 150 ppmv CF_4 , the extrapolation to higher concentration levels are likely to be an underestimation of the actual concentration. The Bomem estimate is manually calculated and should be the most accurate of the three, at 453 ppmv.

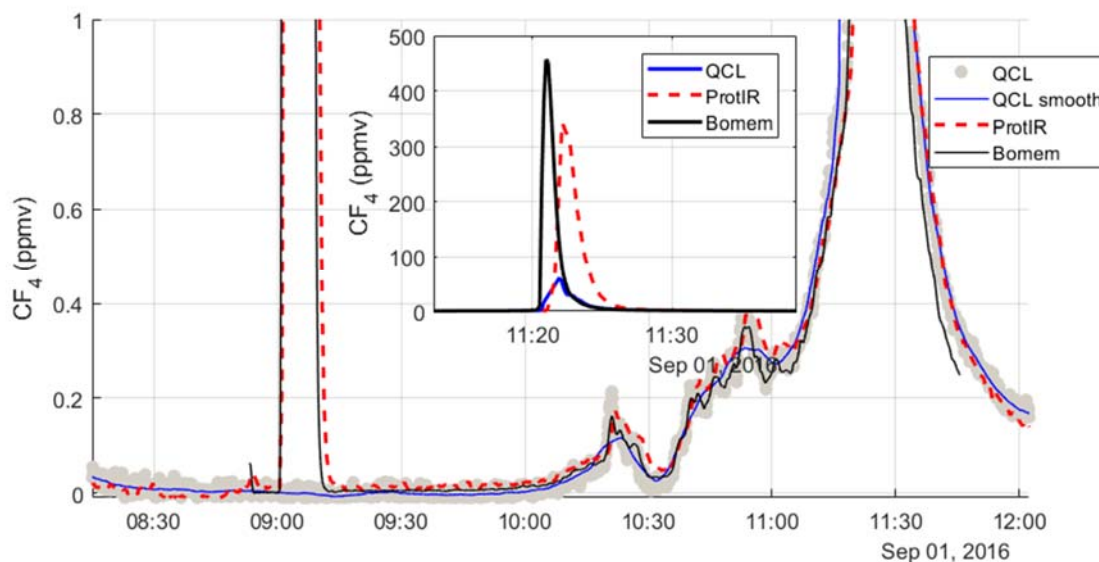


Figure 5. FTIR and QCL concentration estimates prior to and during a full anode effect. The box insert shows the full scale of the ordinate axis. For this time interval, the Bomem was equipped with the 8 meter cell and placed upstream the ProtIR. The ProtIR concentration estimate is therefore trailing that of the Bomem.

At the onset of the anode effect, around 10:00, the CF_4 from the three instruments are fairly consistent, with QCL reporting 15 ppbv, Bomem 13 ppbv and the ProtIR 24 ppbv.

Influence of CH_4

Methane interferes with the single wavenumber used by the QCL. For the FTIR instruments, multiple wavenumbers are available in order to secure interference free quantitation of both CF_4 as well as CH_4 .

Figure 6 shows surface plots of ProIR data of wavenumber ranges for both PFC as well as CH_4 . In order to confirm that the CH_4 estimates are not interference from CF_4 , it was confirmed that an increase in signal at 3015 cm^{-1} was found alongside that of CF_4 at $1220 - 1300\text{ cm}^{-1}$. The gradual increase in CF_4 prior to the full anode effect is also observable around 1281 cm^{-1} . This is not the case for C_2F_6 where a sharp increase in absorbance around 1120 cm^{-1} is observed. This confirms that an increase in CH_4 was observed during the anode effect.

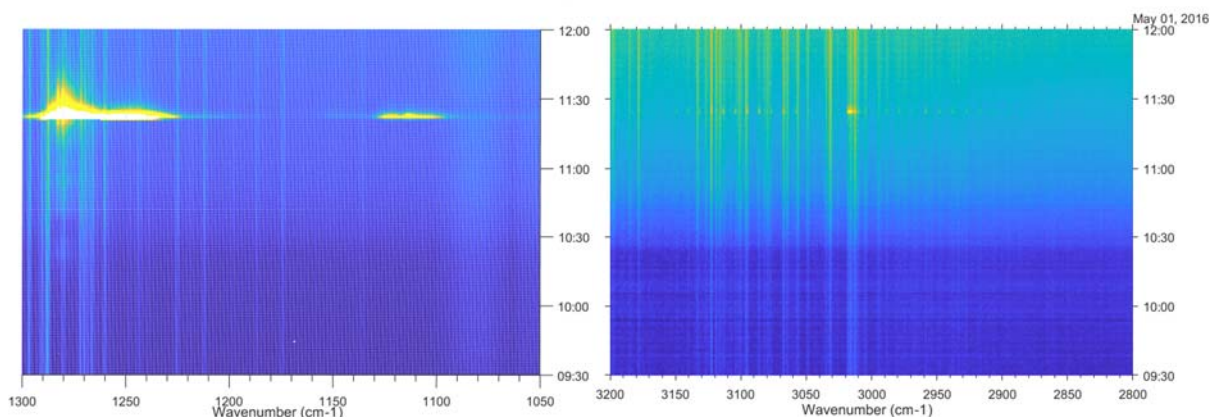


Figure 6. Surface plots of wavenumber ranges representative of PFC (left) and methane (right). Warmer colors indicate higher absorbance. Data was taken from ProtIR instrument.

Concentration estimates of the three species during the full anode effect is given in Figure 7. The methane concentration is fairly stable at 2 ppmv except for during the full anode effect where the concentration increases to about 15 ppmv. Whereas the onset of CF_4 formation is clearly observable more than 60 minutes prior to the full anode effect, the C_2F_6 formation is sharp. It is not known whether this is an effect caused by the lower concentrations of C_2F_6 causing a sudden rise to concentration levels higher than the LOD for the Bomem instrument, for this configuration estimated to be 12 ppbv. The ratio of CF_4 to C_2F_6 at peak value during the anode effect was estimated to around 20 on a molar basis.

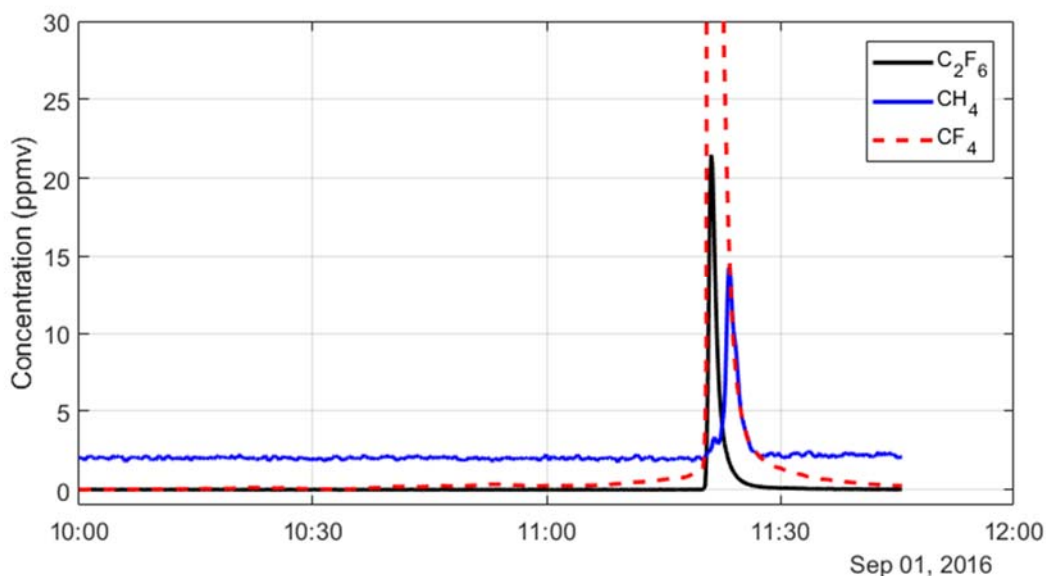


Figure 7. Concentration estimates by Bomem during full anode effect. The peak value of CF_4 (not shown) was 453 ppmv.

Conclusions

For a comparison of the QCL and FTIR analysers it has to be taken into account that the QCL analyser was operated out of specifications with respect to the detection range. However, the results indicate that the QCL analyser is capable of following CF_4 evolution during low voltage anode effects. At concentrations, significantly higher than the detection levels, the QCL shows comparable quantitation to that of the FTIR instruments. As expected, the QCL does not quantify well high CF_4 concentration observed at full anode effects for single cell.

Drift in QCL low concentration was observed compared to the FTIR instruments. It was suspected that the lack of compensation for temperature and pressure changes in the duct could account for some of the observed drift.

Currently, work is performed to optimize the QCL prototype with respect to an increase of the dynamic range so that also higher concentrations will be measured accurately. In addition, a new patent-pending method was developed that will allow in the future to remove interferences of other components in the gas mix (especially CH₄ and H₂O) on the CF₄ concentration measurement.

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