Validation of QCL CF_4 gas analyzer for sensitivity and selectivity

Thor Anders Aarhaug*

SINTEF Industry, NO-7034 Trondheim, Norway

*Corresponding author: taarhaug@sintef.no

Quantum cascade lasers (QCL) has open the mid-infrared (mid-IR) spectral range for laser gas monitors. For perfluorocarbon gases (PFCs) such as CF_4, continuous emission monitors are now commercially available. Since these instruments can only make use of a narrow IR band, spectral interference from other gas species is not easily resolved. In this paper a commercial QCL CF_4 analyser is validated with respect to sensitivity and selectivity. In the laboratory, the laser was mounted on a 0.3-meter measurement cell. A gas mixer provided humidified gas mixtures of CF_4 and methane. The results indicated that while there was no interference from water in the range up to 8000 ppm H_2O, a small interference from methane was observed. This was quantified to be approximately 3 ppb CF_4 per ppm of methane. The sensitivity of the instrument was found to be 10.5 ppb CF_4 for one-meter light path.

Keywords: PFC, perfluorocarbon, emission monitoring, quantum cascade laser

Introduction

PFC emission from primary aluminium production have been significantly reduced from 70 Mt CO_2e equivalents in 1990 to a level of around 35 Mt CO_2e equivalents since 2003. This sustained level is a consequence the increase in annual primary metal production from about 25 Mt in 2003 to about 65 Mt in 2017. Per ton metal produced, the PFC emissions are decreasing. This data is graphed in Figure 1 [1]. With the discovery of PFC emissions not reporting to conventional anode effects came a requirement for quantification of PFC emissions at lower concentrations than before [2].

Extractive Fourier transformed infrared spectroscopy (FTIR) is the most applicable analytical technique for assessment of PFC emissions. With multivariate (e.g. partial least squares) calibration models, robust quantitation with a large concentration working range can be performed. Interference from methane and water can be minimized by using spectral ranges, and sensitivity can be adjusted with gas cell path length. The downside to FTIR spectroscopy is the high maintenance requirements but also a requirement of highly trained operators.

Environmental legislation of PFC emissions may move towards continuous, online monitoring of industrial emissions, and this is one of the 'Tier 3' methods available in the latest Intergovernmental Panel for Climate change (IPCC) Guidelines for greenhouse gas emissions accounting [3]. The motivation for this is to provide better inventory and accounting for the emissions. But online monitoring also provides an opportunity to correlate emissions with the process. In this way, emissions can also be reduced. In the European Union, the best available technology conclusions (BATC) [4] and reference documents (BREF) [5] describes best available technology for reducing PFC emissions. PFCs are expected to enter the EU Emissions Trading System (EU ETS) in the future.

With the advent of quantum cascade laser (QCL) technology, laser type gas analyzers have become available for analytes in the mid-IR spectral range and CF_4 analysers are now commercially available from *NEO Monitors* [6]. With mass production the cost of these instruments is expected to be similar to tunable diode laser (TDL) sensors already existing for HF and SO_2.
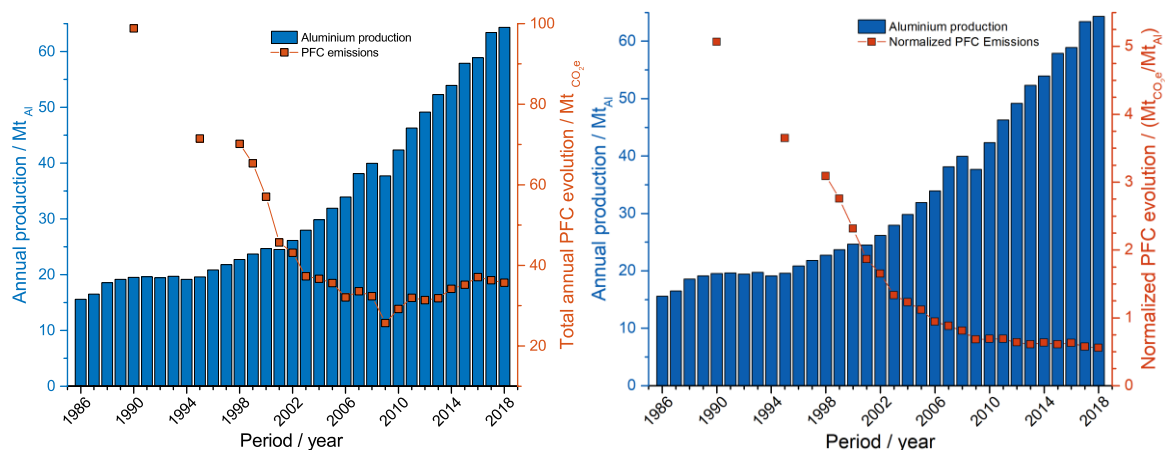

Figure 1. IAI Global PFC emission reporting. Absolute PFC emission values to the left, and normalized PFC emissions (per million t Al) to metal production to the right. Figure made by Henrik Åsheim (Hydro Aluminium) from global emissions data published by the International Aluminium Institute (http://world-aluminium.org).

In this work, the analytical performance of a *NEO Q CF₄* laser is tested for sensitivity towards and interference from water and methane with the aim of evaluating its performance as an online sensor for CF_4 emissions from primary aluminium production. Both methane and water have absorption peaks near the maximum absorption frequency of CF_4 and could therefore interfere when seeking optimal sensitivity for CF_4.

Experimental

A gas mixture of known composition was generated with an Alytech gas mixer [7]. The gas mixture was generated from dilution of nitrogen gas (N_2) with a 5 ppm CF_4 calibration standard (± 2 %). Interferents added to this gas mixture include (a) 1000 ppm methane (CH_4) calibration mixture (± 5 %) and (b) liquid, deionized water (H_2O), using mass and liquid flow controllers respectively. The exit gas from the gas mixer was heat traced to 120 °C so as to avoid condensation of water. The Q CF_4 laser was mounted on a 0.3 m measurement cell for laboratory use. A temperature probe was mounted inside the gas cell to set the correct temperature compensation for the Q CF_4 laser. A *Protea LTD AtmosFIR* FTIR with a 4.2-meter gas cell and a deuterated tri-glycine sulfate (DTGS) detector was installed downstream the laser for validation. A custom-built PLS calibration model was used to quantify CF_4 in the gas. The configuration is illustrated in Figure 2.

Figure 2. Experimental setup with Alytech gas mixer (left), Protea FTIR (right) and NEO Q CF₄ laser (below).

Results and discussion

Instrument bias

NEO has reported 20 ppb.m CF_4 as the instrument's limit of detection (LOD). This translates to 67 ppb for a 0.3-meter cell. Initial testing showed stable readings at 50 ppb, so this was used at the lowest CF_4 concentration setpoint. Readings were recorded for 20 minutes before the CF_4 concentration was increased in steps of 50 ppb to the end point of 250 ppb. The recorded values are shown in Figure 3.
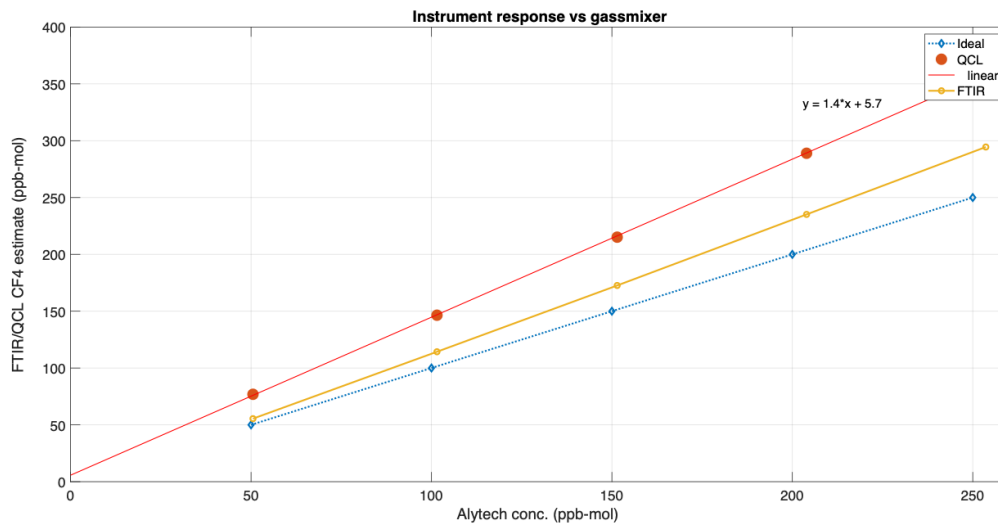

Figure 3. Q CF₄ laser bias estimation. The blue line indicates the true concentration of the gas assuming the gas mixer concentrations are true; red line shows the recorded concentrations by the Q CF₄ laser linearized; yellow line shows the recorded concentrations by the FTIR.

The result showed that the Q CF_4 laser exhibits a concentration dependent bias of about 1.4 times the true value. A small offset of 5.7 ppb that was not concentration dependent was also observed (vertical axis intercept in Figure 3). For comparison, the FTIR showed a smaller deviation from true value with a concentration dependent bias of about 1.2 times the true value.

Interference from water

In order to evaluate the interference from water, water was added to the gas mixture from zero to 8000 ppm in steps of 2000 ppm. At higher water concentrations (above 8000 ppm), condensation of water in the gas was observed. After an initial 30-minute period with pure nitrogen, 50 ppb CF_4 was mixed and fed to the instruments. After 20 minutes, water levels were ramped up to 8000 ppm in steps of 2000 ppm was performed. The sequence is illustrated in Figure 4.
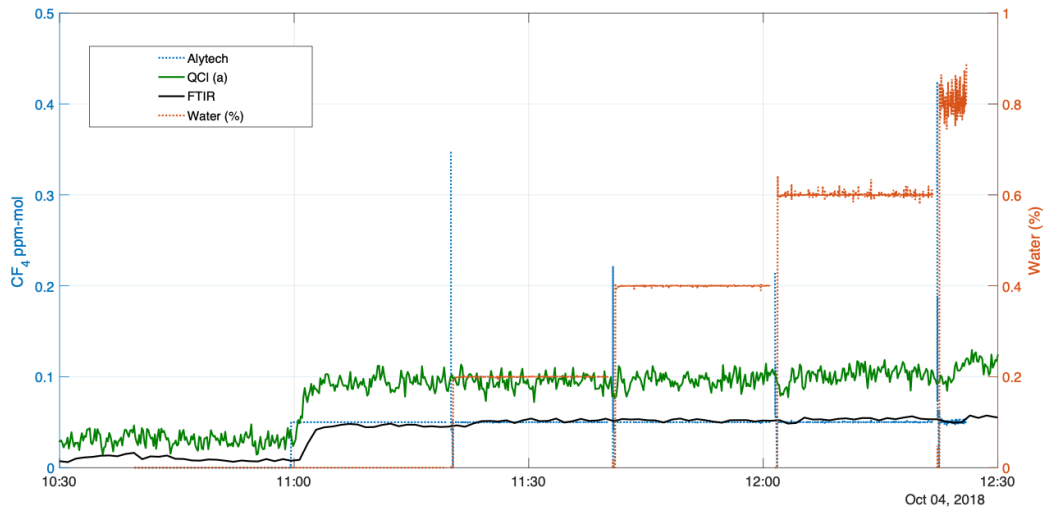

Figure 4. Evaluation of interference from water. Blue curve indicates true CF_4 value; green line indicates Q CF_4 laser concentration estimate; black line indicates FTIR CF_4 concentration estimate; red line indicates true water concentration in gas.

The initial, pure nitrogen sequence showed that the bias for the Q CF_4 (green line, Figure 4) was higher than that of the FTIR (black line). When adding 50 ppb CF_4 into the gas mixture, the Q CF_4 laser recorded values close to 100 ppb whereas the FTIR recorded values are close to the true value. With addition of water, neither instrument showed a significant change in CF_4 concentration estimates. Therefore, at these water concentrations that are relevant for aluminium primary production, interference of water on CF_4 quantitation can be considered to be negligible.

Interference from methane

Interference from methane was evaluated by adding methane to the CF_4 gas mixture, at levels ranging from 0 to 40 ppm. Methane in emissions from aluminium primary production has been reported previously by Espinoza-Nava et al.[8] – concentrations can be stable in the 3-4 ppm range in the stack gas of gas treatment centers (GTCs). Aarhaug et al.[9] showed however that during conventional anode effects (i.e. those occurring at cell voltage above 8 V), methane concentrations could increase from 2 ppm to 20 ppm in the gases from a single cell. The concentrations selected in these experiments were chosen to as exaggerate the effect of any methane interference but also to include the range of methane concentrations expected in cells, so that any interference could be quantified.

The sequence was started with nitrogen, followed by 50 ppb CF_4 before the methane concentration was ramped up in steps of 10 ppm. The sequence is illustrated in Figure 5.
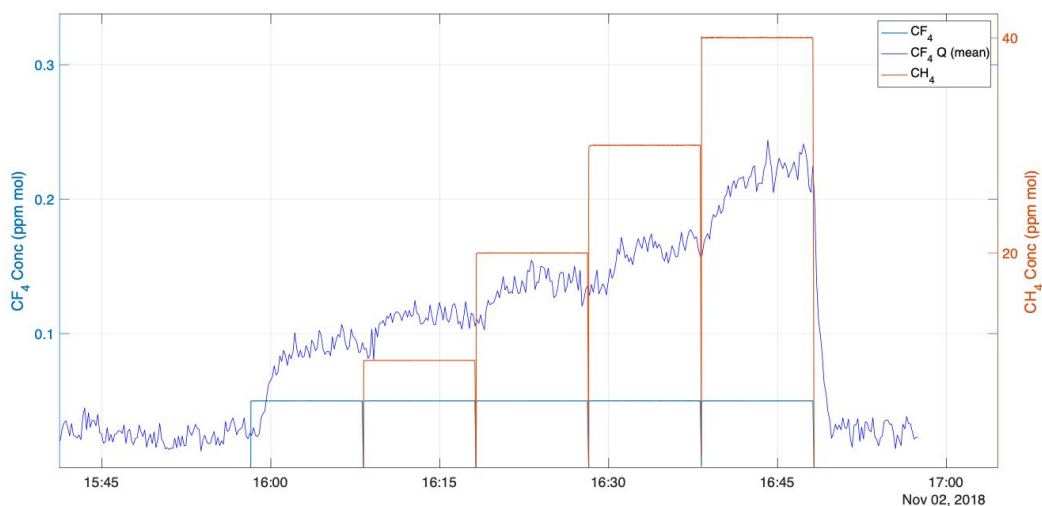
Figure 5. Interference from methane. True values of CF₄ (blue) and methane (red). Q CF₄ response (smoothed) in light blue.

The results clearly indicate interference from methane on the CF_4 concentration estimate. Increasing methane concentration from zero to 40 ppm doubles the CF_4 concentration estimate. By linear regression, the interference was estimated to be in order of 3.1 ppb CF_4 per ppm CH_4 present in the gas.
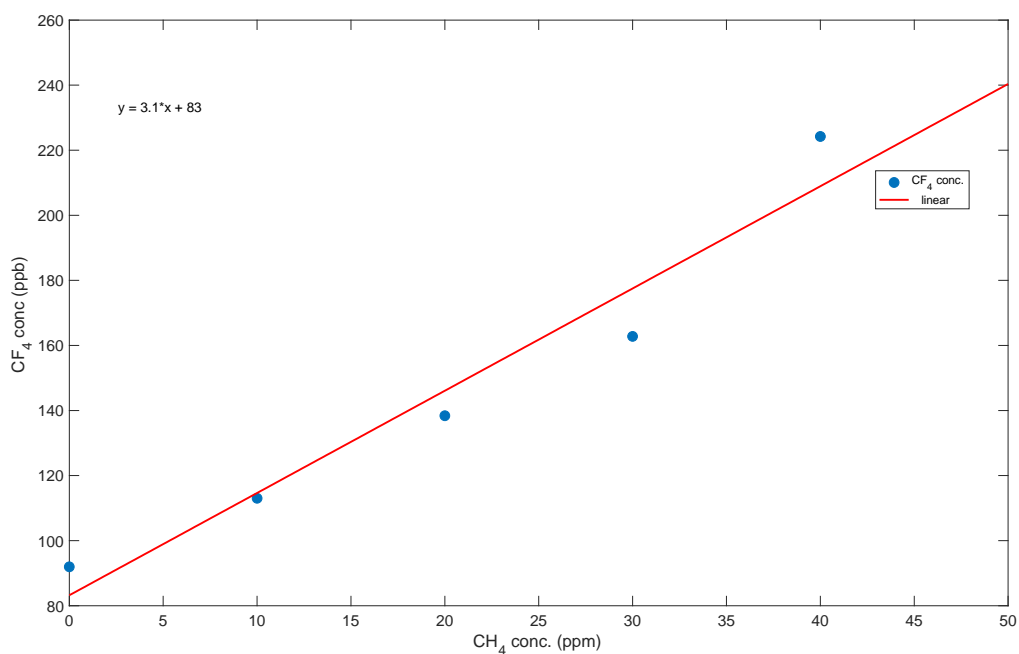

Figure 6. Quantification of methane interference.

The spectral interference at the frequency used for the QCL laser can be illustrated with the FTIR spectral data. The Q CF_4 laser uses a peak near 1283 cm^{-1} for quantitation. Spectra recorded with the FTIR is shown in Figure 7.
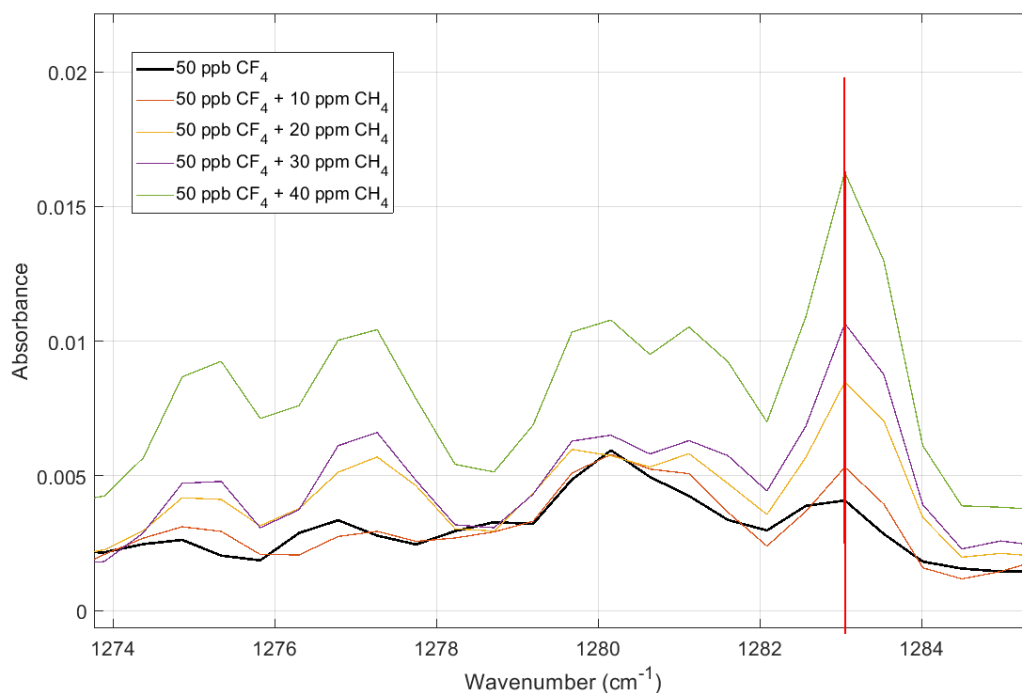
Figure 7. Specific IR absorbance vs. wavenumber plotted for several concentrations of CF_4 and CH_4. The red vertical line indicates the wavenumber used by QCL laser.

The spectra show that an increase in the methane concentration increases the absorbance at 1283 cm^{-1}. The FTIR uses a band of frequencies in the quantitation that does not include interference from methane.

Sensitivity

The sensitivity of the instrument was evaluated from the IUPAC definition of LOD [10] which is 3 standard deviations (+3σ, 16 ppb) above the blank mean value. After stable reading of the instrument in pure nitrogen was obtained, 50 repeat readings were recorded from which the blank mean value was calculated. 3 standard deviations of the blank were added to the blank mean value, 19 ppb. The LOD was estimated to be 35 ppb, or 10.5 ppb*m. The data for LOD estimation is shown in Figure 8.
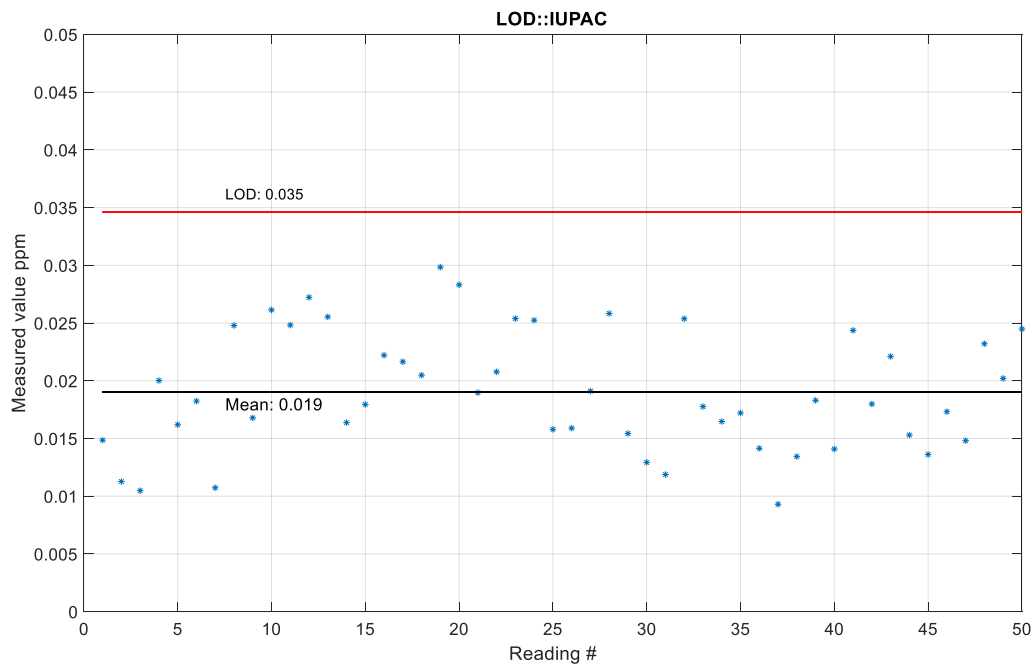
Figure 8. LOD estimation using the IUPAC definition, based on the mean blank value + 3 standard deviations.

Conclusions

A QCL type CF_4 monitor manufactured by *Neo Monitors* has been tested for analytical performance and for selectivity in the presence of relevant impurities. The instrument showed a concentration dependent bias of 1.4. The bias was found to be linear and could be corrected for. The instrument was checked for any interference from humidity levels in the gas relevant for primary aluminium production, and no interference was detected. However for methane, an interference of about 3.1 ppb CF_4 per ppm methane was observed. Assuming constant methane levels in the pot gas emissions, this could easily be corrected for. It has however been shown that the methane concentrations can increase during conventional anode effects, so the characteristics of methane emissions should be investigated. This could be done by adding a methane gas laser to the gas treatment center stack. Finally, investigations of the instrument sensitivity in the laboratory (with a 0.3-meter gas cell) found a limit of detection (LOD) of 35 ppb. Normalized to a 1-meter cell length, this LOD estimate becomes 10.5 ppb*m. For example, in a 2-meter diameter stack, this would translate to a sensitivity of just over 5 ppb under ideal conditions. The actual performance of the laser should be evaluated under real conditions for a time period of at one least week.

References

1.   Henrik Åsheim. *PFC evolution in the aluminium production process*, in *Department of materials science and engineering*. PhD Thesis, 2017, NTNU.
2.   Jerry Marks and Chris Bayliss. *GHG measurement and inventory for aluminium production.* Light Metals, 2012: p. 805-808.
3.   Intergovernmental Panel for Climate Change. *Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*. 2019: https://www.ipcc-nggip.iges.or.jp/public/2019rf/index.html.
4.   European Commission. *Best available techniques (BAT) conclusions under Directive 2010/75/EU*. 2016; Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2016.174.01.0032.01.ENG.

5.   European Commission. *Best available techniques (BAT) reference document for the non-ferrous metal industries.* 2017.

6.   NEO Monitors, http://neomonitors.com/tdls-dust-and-gas-analyzers/lasergas-q-cf4/, Visited 1.10.2019.

7.   Alytech, https://gasmix.com/, Visited 1.10.2019.

8.   Luis Espinoza-Nava, Nicola Menegazzo, Neal R. Dando and Peter Geiser. *QCL-based perfluorocarbon emission monitoring.* Light Metals, 2016: p. 541-544.

9.   Thor A. Aarhaug, Alain Ferber, Heiko Gaertner, Steinar Kolås, Sven Olof Ryman, Peter Geiser. *Validation of online monitoring of PFC by QCL with FTIR spectroscopy.* Light Metals, 2018: p. 1487-1493.

10.   International Union of Pure and Applied Chemistry. *Gold Book* 2019.