

A Review of Equipment for Accurate PFC Measurements

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Abstract

To obtain reliable perfluorocarbon (PFC) measurement results requires expertise and competence in the measurement methodology and knowledge of the smelting technology. We enumerate different measurement methods that have been used to measure PFC emissions. The Fourier Transform Infrared method is the most versatile of all the methods and gives the most information about the smelting process. It has the best temporal resolution making 10 interferometer scans each second and can measure low voltage emissions at the same time as anode effect emissions. Both authors have extensive experience measuring PFC emissions (CF₄ and C₂F₆) at aluminum smelters worldwide. We will present available measurement technology with a checklist to ensure accurate and reliable measurements.

Keywords: Perfluorocarbon (PFC), Tetrafluoro methane CF₄, Hexafluoro ethane C₂F₆, Anode effect, High and low voltage PFC emissions.

1. Introduction

The perfluorocarbon gases (PFCs) tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆) are known greenhouse gases (GHG) with long atmospheric lifetimes, estimated at 50 000 and 10 000 years, respectively. These trace gases are linked to global warming due to their ability to efficiently absorb infrared radiation. The global warming potentials (GWP) of these gases are reported as CO₂ equivalents (GWP of CO₂ = 1). Every kilogram of CF₄ or C₂F₆ emitted is equivalent to 7 380 kg CO₂ and 12 400 kg CO₂, respectively [15].

PFC emissions occur during a condition known as an anode effect (AE), an event that occurs when the ore (Al₂O₃) concentration in the electrolytic bath drops below ~ 1 %, the pot voltage rises, and the bath and carbon anode(s) begin to react. The 2019 Refinement to the 2006 IPCC Guidelines includes CF₄ and C₂F₆ emissions coming from high voltage (HV), low voltage (LV) and pot start-up PFC emissions. The refinement includes updated values for Tier 1, Tier 2 and Tier 3 methods that can be used to calculate PFC emission depending on the pot technology and if facility specific data per technology are available [1]. The International Aluminum Institute (IAI) published a PFC measurement guideline with a review of all methodologies to accurately account for high-voltage PFC emissions, produced when the pot voltage is above 8 V, and low-voltage PFC emissions, produced when the pot voltage is below 8 V [2]. Any PFC reporting protocol will require reporting total PFC emissions, including LV PFC emissions. LV PFC emissions occurred during pot room operation activities such as anode changes, tapping, pot starts, underfeed periods, and high pot noise periods [3–5]. Any localized increase in pot voltage can induce PFC emissions from the pot. During anode changes, LV PFC emissions occur when anode current distribution is unbalanced, and the critical current density is reached on one or more of the anodes that have been subjected to alumina depletion.

The International Aluminum Institute (IAI) gas initiative has launched a long-term gas emission reduction target by December 2024 and to identify an interim greenhouse gas emission reduction

milestone, ideally by 2030, to ensure early progress can be tracked for all its members. This initiative was launched at the United Nations's Climate Change Conference (COP 28) in Dubai [6]. To accomplish this goal, it is recommended that the aluminum industry report total PFC emissions on an annual basis. We recommend direct measurement by real time extractive sampling for Tier 3 reporting offers the most efficient and accurate technique giving all PFC emissions.

2. How to Decide Which Equipment to Use to Measure Total PFC Emissions

The best approach to measure PFC emissions depends on the main objective of the PFC measurement campaign. The decision to use monitoring equipment relies on if the objective is for GHG inventory, e.g., total PFC emissions reporting or for process improvement like LV PFC emissions reduction or benchmarking. To define root cause mechanisms and eliminate or reduce LV PFC emissions, a proper understanding and quantification of how pot operations impact these non-desired emissions are required for accurate PFC accounting to enable appropriate countermeasures. LV PFC emissions can contribute from 5 to 80 % of overall PFC emissions from smelting locations, depending on anode effect performance, pot operation and size, and work practices. Process data cannot predict and estimate LV PFC emissions. Solutions for comprehensive PFC reporting require the use of continuous monitoring or time-integrated sampling in canisters during a period. This measurement period should be ideally selected to be representative of each potline in all smelters. Thus, when emissions are being measured for compliance or determination of site emissions, one would choose as large a section of pots as possible. For process improvement a small section of pots or even a single pot might be sampled. The PFC concentrations will vary from parts per billion for a large section of pots to tens, or even hundreds of parts per million for a small section of pots when conducting process improvement research.

The ideal monitoring technique should provide the most information to measure and manage to reduce PFC emissions. There are four main techniques to use to measure PFC emissions.

3. Analytical Techniques

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR has been one of the preferred techniques to measure and report GHG inventories as well as measure and manage PFC emissions to gain process improvements. The main advantage of FTIR spectroscopy is the simultaneous measurement of most gases coming from a smelter pot exhaust, which gives additional emission information. Furthermore, spectral data can be reprocessed to verify CF_4 and C_2F_6 emissions at different ranges e.g., single part-per-billion to hundreds of parts-per-million concentrations, which can occur from single-pot or a section of several pot exhausts. FTIR requires extractive sampling with filters to avoid instrument intensity degradation, corrosion of internal optics, and might need maintenance during measurement campaigns. FTIR is a reliable technique, but it can drift over time and needs to be accurately calibrated in the low ppb range [7]. Another advantage of doing a FTIR continuous measurement for a limited time is to develop coefficients to calculate HV and LV emissions simultaneously without waiting from an analytical lab to get results if canisters samplers are used.

For smelters measurements a small table is needed to place the instrument and laptop as shown in Figure 1.



Figure 1. FTIR instrument.

3.2 Canister Sampling with Subsequent GC-MS analysis

Canisters are well suited for the collection and analysis of volatile organic compounds like EPA method TO-15. However, not all trace-level greenhouse gases are included on the standard lists of targets ‘air toxics’ referenced by TO-15 and TO-17. Tetrafluoro methane, CF_4 , and hexafluoro ethane, C_2F_6 (boiling point $-128\text{ }^\circ\text{C}$ and $-78\text{ }^\circ\text{C}$) are not on the list and a standardized method is needed. However, the use of canisters to collect PFC emissions over a specific time has been tested and results were reported lately by Alcoa and Hydro [7, 8].

The method uses evacuated canisters, which are supplied with a negative pressure (approximately -30'' Hg or -1015 hPa), in a 6 Liter container. Canisters are supplied with a pre-set flow restrictor/controller and particulate filter (the restrictor controls the flow of air into the canister to do time integration sampling). Once connected to the sample point, gas is drawn into the canister by opening the valve. Laboratory analysis is completed using GC-MS by sending the canister to qualified environmental laboratories. Use of Thermal Desorption cold trap allows parts per trillion CF_4/C_2F_6 detection limits [9].

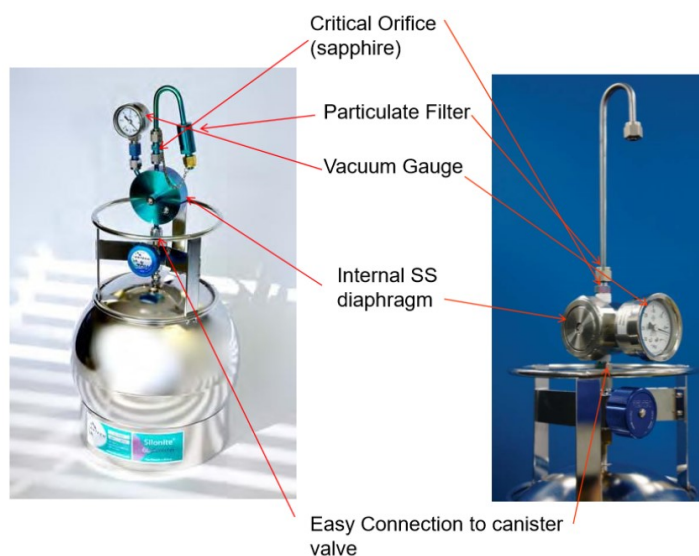


Figure 2. 6 Liters canister for PFC sampling.

The main advantage of Canisters is that they can be used from multiple emission sources like several stacks in multiple potlines. Apparently, it is simpler sampling, uses less equipment, reduced cost, and advanced expertise is not needed to report total PFC emissions but lacks the continuous information provided by FTIR. Furthermore, the extra analytical required GC-MS analyses will add more cost into the sampling campaign.

3.3 Quantum Cascade Laser

Quantum cascade lasers (QCL), which are used in the mid-infrared region and are now commercially available, can be installed at the duct, have few interferences, and might have the required detection limits to measure all PFC emissions continuously. Few smelters tested the QCL at an exhaust outlet and compared it during a short period with FTIR spectroscopy given a bias of approximately 10 ppb (parts per billion) [10]. This technology can be an option for installation in the exhaust duct stack that collects hundreds of pots to track total PFC emissions over long periods. However, this development technology requires checking instrument drift, long-term durability of the laser source, and comparison with FTIR and canister sampling and GC-MS analysis over a long period.



Figure 3. QCL emitter installed at duct.

3.4 Photoacoustic InfraRed

Infrared instruments based on photoacoustic detection have been previously used for PFC emissions monitoring when FTIR were not suitable to measure high PFC emission from Soderberg smelters. We used an IR Photoacoustic system from California Analytical Instruments (Model 1412) configured for bench-top operation, which provided measurement of PFC emissions using a calibration with an interference matrix. However, instrument sensitivity was not capable of measuring low ppb PFC emissions due to inadequate sampling frequency.

Another photo-acoustic analyzer from Mirsense is now commercially available for several gases (up to 4 gases simultaneously on the same analyzer, with 4 lasers at the appropriate wavelength). Rio Tinto is developing a low-cost analyzer with a sampling system to carry the gas in the chamber on the analyzer [11]. They are still working on this because they want a system able to work for months without any maintenance. Nevertheless, a comparison with FTIR will ensure the IR Photoacoustic can have similar detection limits for CF_4 and C_2F_6 .

4. Considerations to Measure PFC Emissions Using FTIR Spectroscopy

4.1 PFC Sampling Layout

The sampling line configuration used for measurement of PFCs is shown in Figure 4. The sampling probe is placed either in the inlet or outlet duct of a dry scrubber for a series of pots or at the duct of one individual pot.

If the measurement is for PFC reporting purposes, Anode Effect Frequency (AEF) is used to decide how many pots can be measured, the number of measurement days, and the number of anode effects that will be representative of the anode effects duration distribution. For example, a 3–5-day measurement time with AEF = 0.1, that collects the emissions from 100–150 pots, will provide > 50 anode effects. A chart of anode effects distribution during the measurement will be compared with typical plant anode effect duration distribution to evaluate if the sampling was representative and to calculate both CF_4 and C_2F_6 emissions factors as well as low voltage PFC emissions. While in some technologies each anode effect lasts several minutes, in others, the typical duration is just a few seconds. Because FTIR can scan at a fast rate, 10 interferometer scans each second, short anode effects are effectively detected by FTIR having a great advantage over other techniques.

If the measurement is to improve process control like optimization of feeding parameters and/or assessment of LV PFC emissions during anode changes to reduce LV PFC emissions, single pots are measured by placing the probe in the exhaust duct. Therefore, one measurement campaign can be made to vary different process conditions to establish which one produces the lowest PFC emissions. Multiple FTIR will reduce the time to measure all conditions as several single pots, usually 4–10 pots, will be measured simultaneously. It is also important to select close by pots in the process study to minimize the required tubing to extract the exhaust gas emission from each pot to the FTIR inlet. The study could take up to 1–3 weeks, and the best process condition, with the lowest PFC emission, can be expanded to several pots to compare key process indicators between the test section and the normal operating section [12–14].

Figure 5 shows a typical CF_4 concentration emission over a measurement period of several days. It is also important that the entire sampling line is vacuum checked prior to the start of sampling to ensure that there were no leaks in the sampling line during the measurement period. The FTIR gas cell is heated to approximately 80–120 °C to minimize condensation on internal optics. The data collection parameters are usually set at 10–30 seconds/scan and 2.0 cm^{-1} resolution. This time is necessary to capture very short duration anode effects. A reference spectrum of dry nitrogen (obtained from local gas supplier) is used to calculate absorbance spectra from single-beam FTIR files.

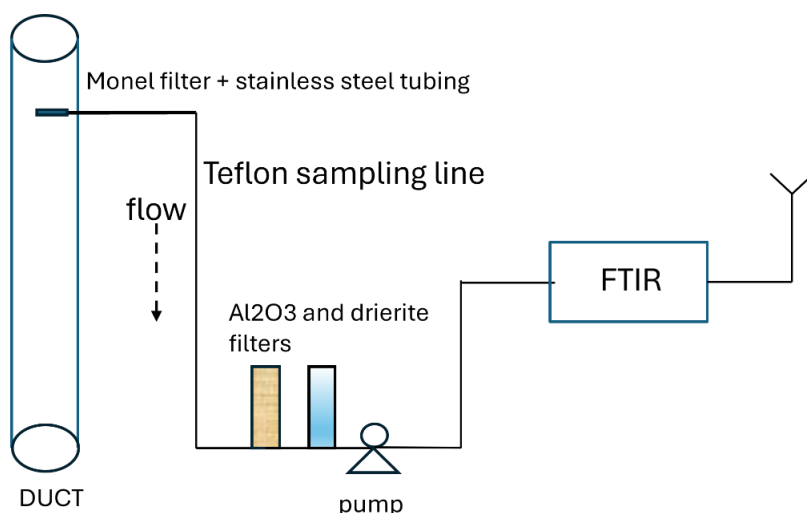


Figure 4. Layout of PFC sampling (not to scale).

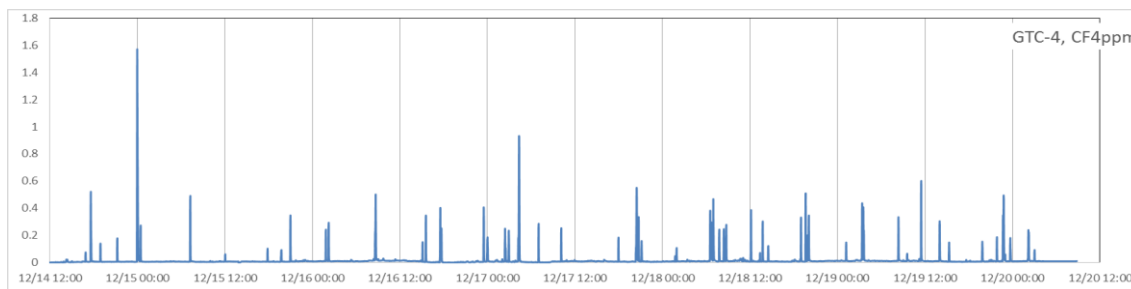


Figure 5. Typical CF₄ concentration results in parts-per-million over measurement period.

4.2 FTIR Instrument Parameters Setting to Increase Sensitivity [2]

The infrared spectrum of the sample in the FTIR gas cell is measured and stored on a computer. Absorbance band intensities in the spectrum are related to sample concentrations by what is commonly referred to as Beer's Law:

$$A_i = a_i b C_i \quad (1)$$

where:

- A_i Absorbance at a given frequency of the i th sample component
- a_i Absorption coefficient (absorptivity) of the i th sample component
- b Path length of the cell
- C_i Concentration of the i th sample component.

The instrument should be calibrated in the range for expected CF₄ and C₂F₆ emissions. The requirement is to measure CF₄ in the 0.010–10 ppm (parts per million) and C₂F₆ in the 0.020–1 ppm range. Simultaneous pot starts might require extending the range to 100 ppm CF₄ and 10 ppm C₂F₆.

FTIR manufacturers offer configuration options for the optical path in gas cell, detector, and resolution. Any third-party company should state FTIR instrument make and model, cell pathlength and how low CF₄ can be detected and provide infrared spectra that shows CF₄ absorbance band low detection at 1283 cm⁻¹ and C₂F₆ absorbance band detection at 1250 cm⁻¹. It is recommended to use a cell pathlength from 4 m to 10 m to allow both CF₄ and C₂F₆ to be measured at the parts-per-billion range.

Primary gas standards are required to be certified within 2 or 5 % accuracy. Secondary standards are necessary to verify primary calibrations and to dilute concentrations to low ppb concentrations. All third-party companies should provide a certificate of analysis for the gases used in the CF₄ and C₂F₆ calibrations.

Infrared absorption spectroscopy is performed by directing an infrared beam through a gas cell to a detector. The frequency-dependent infrared absorbance of the sample is measured by ratioing this detector signal (sample single beam spectrum) to a signal obtained without a sample in the beam path (background single beam spectrum) to obtain the absorbance of the sample. This sample absorbance is directly proportional to its concentration as shown in the Beer Law equation.

Nitrogen is used as a zero background because it is inert and does not show any absorption in the infrared. When nitrogen is used as a sample and background simultaneously by combining two background single beam spectra it is called a one hundred percent line. Ideally, this line is equal to 100 % transmittance (or zero absorbance) at every frequency in the spectrum. Practically, a zero-absorbance line is used to measure the baseline noise in the spectrum. Thus, FTIR

instruments can provide a Signal to Noise Ratio spectrum and value, which determines how the instrument sensitivity is to measure low concentrations. Any third-party company should state the limit of detection of both CF₄ and C₂F₆.

4.3 Common Mistakes that Can Be Avoided when Hiring Third-Party Companies

The checklist below identifies some comments and recommendations that can impact reliable results when measuring PFC emissions [2]. These are provided as an example of ‘things to check’ when liaising with third-party companies:

- Instrument resolution, gas cell Length, detector, calibration standards, QA/QC during sampling, data processing should be provided.
- Anode Effect Frequency (AEF)/Anode Effect Duration (AED) should be recorded and statistically compared between short-term measurement vs plant AEF/AED performance to make sampling representative.
- Any FTIR drift, for example shown in zero baseline, will compromise CF₄ and C₂F₆ sensitivity over periods of time to detect low voltage PFC emissions. Hence FTIR drift must be avoided specially to detect low concentration trends in LV PFC emissions.
- Perform Nitrogen backgrounds daily and use Nitrogen scans as sample to evaluate sensitivity and verify instrument can distinguish between zero CF₄ and 10-50 ppb of CF₄.
- Evaluate linearity of calibration so that high/low concentrations can be recalculated after measurements. This involves periods of zero PFC emissions and during new pot starts.
- Another recommendation is to collect gas bags during stable low concentration periods to validate FTIR data with another FTIR instrument or with GC-MS.

5. Discussion

FTIR is the most robust and the one which gives the most valuable information from all four techniques described above. Quantum Cascade Laser (QCL) must prove it can give the same information over longer periods and be maintenance free. It might be placed at the common exhaust stack to measure total PFC emissions. Photoacoustic development is still ongoing, comparisons are needed to prove it can track LV PFC emissions as FTIR and QCL.

While the canister method provides a total (HV +LV) PFC emission measurement, there are many smelters facilities that may not want to invest the time and money to set up continuous sampling and sending these samples off for analysis. Previous work by Hydro, where they attempted to calculate a “slope” that included HV and LV emissions, might not be accurate and not give the extra information that the FTIR can provide. Even though the canister methods might be less expensive than the FTIR measurement, a real estimate should be done at facilities that have many exit stacks. FTIR can also do an integrated sample into a bag if that is desired.

The FTIR also allows to review each anode effect by anode effect analysis of the data, which then allows a tier 3 non-linear analysis of the data which will provide a much more robust way of constructing emission inventories. It has been authors experience that it is impossible to get anode effect duration distribution in a limited period that holds over a three-year period. There is always a particular pot behavior that throws the distribution off – particularly due to long duration anode effects. A few of these long duration events will throw the average anode effect minutes/pot-day off. The slope calculation is subject to move in correlation with the average anode effect minutes which are greatly affected by long anode effects.

6. Conclusions

The Fourier Transform Infrared method is the most versatile of all the methods and gives the most information about the smelting process. It has the best temporal resolution making 10 interferometer scans each second and can measure low voltage emissions at the same time as anode effect emissions. Additionally, FTIR can measure other gaseous carbon compounds simultaneously with the PFCs and duct flow rates can be calculated from the potline net carbon consumption figure. The results are available immediately and there is no need to ship samples and wait for results.

The capital investment of FTIR and sampling equipment may be paid off by process improvements that can be obtained by reducing PFC emissions. Therefore, more metal can be produced by avoiding the generation of LV PFC emissions during anode changes, feeding improvements, or avoiding any pot instability that will lead to better pot performance.

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