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Good Practice Guidance: Measuring Perfluorocarbons

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International Aluminium Institute (IAI)

Current IAI membership represents over 60% of global bauxite, alumina and aluminium production. Since its foundation in 1972, members of IAI have been companies engaged in the production of bauxite, alumina, aluminium, the recycling of aluminium, fabrication of aluminium, or as joint venture partners in such. The key objectives of IAI are to:

- Increase the market for aluminium by enhancing world-wide awareness of its unique and valuable qualities;
- Provide the global forum for aluminium producers on matters of common concern and liaise with regional and national aluminium associations to achieve efficient and cost-effective cooperation;
- Identify issues of relevance to the production, use and recycling of aluminium and promote appropriate research and other action concerning them;
- Encourage and assist continuous progress in the healthy, safe and environmentally sound production of aluminium;
- Collect statistical and other relevant information and communicate it to the industry and its principal stakeholders; and
- Communicate the views and positions of the aluminium industry to international agencies and other relevant parties.

Through the IAI, the aluminium industry aims to promote a wider understanding of its activities and demonstrate both its responsibility in producing the metal and the potential benefits to be realised through its use in sustainable applications and through recycling.

The IAI would like to acknowledge the following companies for their review and contribution to these guidelines.

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Disclaimer: The information contained in this publication is presented to the best of the IAI’s knowledge but is without warranty. The application of the methods, procedures and processes for perfluorocarbon measurement outlined in this publication is beyond the IAI’s control and responsibility and should be taken in compliance with local and national regulatory requirements.

Preface

The USEPA/IAI Perfluorocarbon (PFC) Measurement Protocol was first introduced in 2003 and subsequently updated in 2008 to provide guidelines for accurate and comparable measurement data for PFC emissions from electrolytic primary aluminum production. Since the 2008 update there have been major changes in the reduction cell technology and methodologies for estimating and reporting PFC emissions as part of national greenhouse gas inventories.

Modern reduction cell technology involves much larger cells that operate with more than 32 anodes, line currents of 360 to 600 kiloamperes, and reduced anode to cathode distances to lower power consumption. These changes have resulted in changes to the PFC emissions associated with certain technology types. PFC emissions have historically been directly linked to process upset conditions known as anode effects that occur in the cell. Broadly, modern reduction cell technology can be grouped into two categories – those which operate with automated process control systems that take actions to “kill” the anode effect rapidly, often in only a few seconds, and, those where manual actions are required to “kill” the anode effect.

PFC measurements made on the modern cells (of both groupings outlined above) brought to light the fact that PFC emissions can, and do occur, outside those times when the cell is on anode effect with average cell voltage exceeding the defined trigger voltage; eight volts for many cell technologies. This realization has resulted in redefining these emissions into two categories - high voltage (HV) PFC emissions and low voltage (LV) PFC emissions. HV emissions can be estimated from the anode effect process data recorded by smelter operators, whilst LV emissions are not directly related to recorded anode effect process data, or, any recorded process data. PFCs from cell start up (CSU) is also included in the update to improve completeness of the inventory estimates.

The 2008 USEPA/IAI Measurement Protocol only covered HV emissions. This 2020 update is intended to provide practical guidance for sites measuring and reporting all PFC emissions. It incorporates the specification still relevant from the 2008 Protocol and additionally, the latest information on the main methods for measuring LV, HV (including cell start-up, CSU) PFC emissions as outlined in the 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. It describes how to:

1. Measure HV PFC emissions (including CSU) and LV PFC emissions based on the latest information and technology and with consideration of the main objective of the measurement campaign;
2. Distinguish between HV and LV emissions; and
3. Calculate and report HV and LV PFC emissions consistent with the 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.

It should be noted that the updated information provided in this Guidance reflects the latest knowledge on LV and CSU PFCs which is relatively new and still under development. The information is intended to provide guidance to smelters following the update to the IPCC National GHG Inventory Reporting Guidelines, and care should be taken with regards to regulatory reporting which often stipulate specific methods. The methodologies presented here for LV and CSU PFC emissions are intended to provide high level estimates as knowledge on LV PFC and start-up PFC emissions continue to evolve. The industry continues to work on improving the methodologies for measurement and reporting PFC emissions.

Contents

1. Introduction and Background

1.1 Objectives

The primary objective of these guidelines is to outline good practices to assist smelters in the measurement and reporting of high voltage (HV) PFC emissions (including cell-start up, CSU) and low voltage (LV) PFC emissions. It is intended that this guidance provides practical information that will assist in establishing reliable PFC emission factors or measurement data for PFC emissions from aluminum smelters, as defined in Volume 3, Chapter 4.4 of the 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.

Broadly, there are two major purposes for measuring PFCs and establishing emission factors:

- **Meeting reporting requirements** – Some countries have regulations that require reporting of PFC emissions from aluminium smelters. In some cases, this includes meeting established reduction targets or national GHG inventory requirements over time.
- **Process improvement and benchmarking** – Smelters are continually working to refine the reduction process and to improve performance. Reducing PFC emissions has been an industry focus since the early 1990s and much progress has been made. Reliable measurements also allow for the comparison of emissions levels with other smelters.

The best approach to adopt for measuring PFC emissions may be dependent on the main objective of the PFC measurement campaign. A decision tree is included below to guide users in identifying an appropriate methodology for each objective. The decision tree considers the most efficient and cost-effective options based on current needs. It should be noted that for regulatory reporting, specific methodologies are sometimes stipulated, and operators should align with those requirements. The decision tree covers three distinct methods however these could be adopted in combination as necessary:

- **Method 1:** Direct Measurement by continuous monitoring (e.g. laser) for an extended period.
- **Method 2:** Direct Measurement by real time extractive sampling (e.g. FTIR) for a limited period, typically 72 hours when AEF >0.1 AE/pot/day.
- **Method 3:** Direct Measurement using an average sample collected over a limited period (e.g. canister, bag) and projecting results to extended periods.

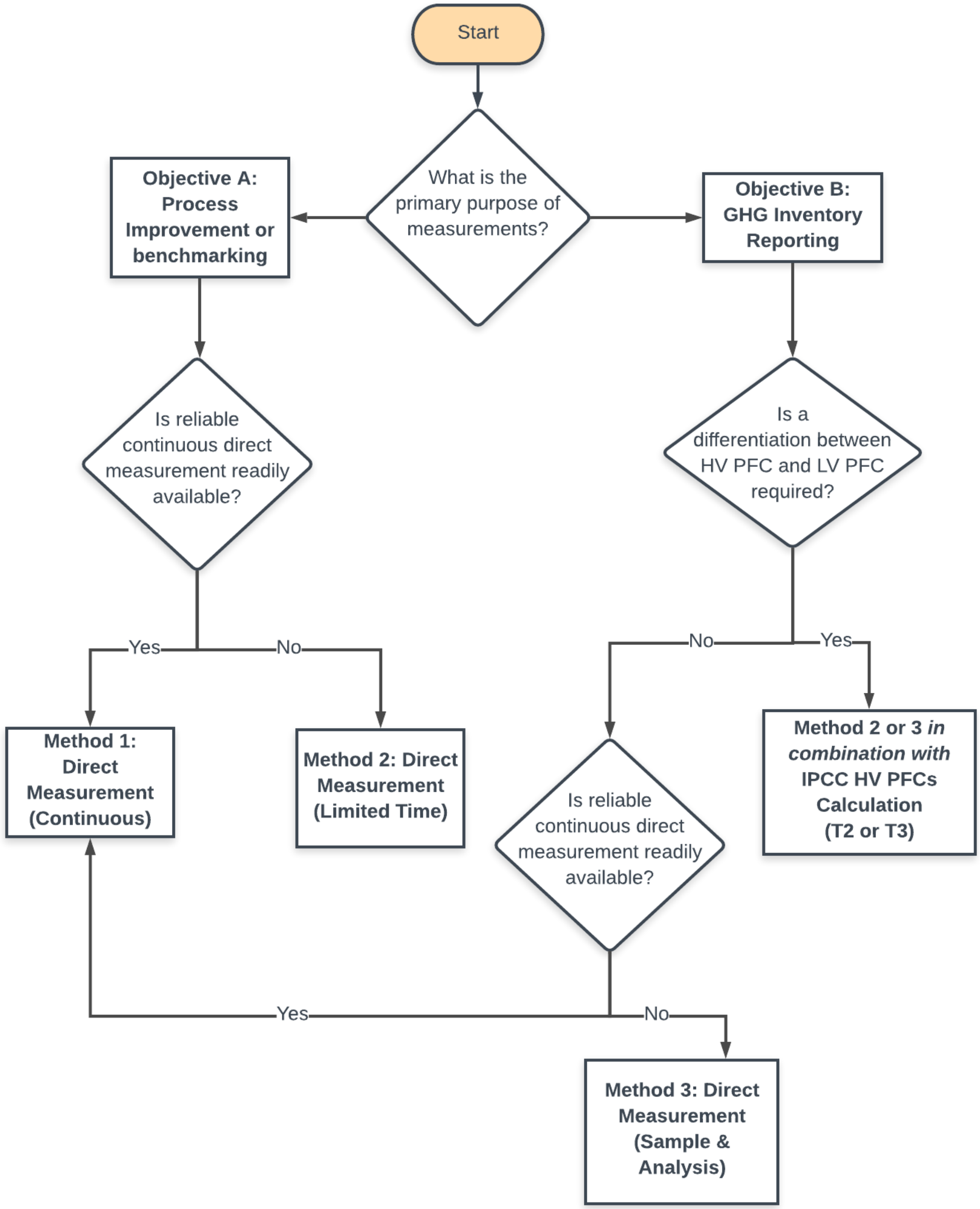

Figure 1: Decision tree to assist in identifying best suited methodology(ies) based on the primary objective requirements and availability of suitable technology or expertise. It should be noted that all methods could be used for total emissions reporting but may not be practicable. For regulatory reporting there may be prescribed methodologies set out in regulation.

1.2 Key Definitions

For the purposes of this document the following definitions will apply.

Term	Definition
PFC emissions	The emissions of tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) from upsets in the electrochemical reduction of alumina to aluminum. While traces of octafluoropropane (C_3F_8) have been reported in at least one study (Fraser et al. 2003), possible levels of this compound are insignificant compared with emissions of CF_4 and C_2F_6.
Total PFC emissions	The sum of PFCs related to high voltage (HV) emissions, low voltage (LV) emissions and Cell Start Up (CSU) emissions as is noted in Equation 4.24A in the 2019 Refinement to the 2006 IPCC Methods for National Greenhouse Gas Inventories.
High Voltage PFC emissions (HV)	PFC emissions resulting from anode effects. An anode effect is a process parameter typically recorded by smelters where the average reduction cell voltage exceeds a facility-defined trigger voltage, for a specific period of time (Wong et al. 2019). Neither the trigger voltage nor the time period for which the voltage must be exceeded are universally established parameters, but the 2019 IPCC Guidelines refers to the most often quoted definition of *8 volts for >3 secs*. HV PFC emissions have been shown to increase with the time a reduction cell exceeds the trigger voltage in a non-linear manner.
Low Voltage PFC emissions (LV)	Emissions of PFC gases under process conditions where the average cell voltage does not exceed the site-specific trigger voltage. There has been extensive research on the mechanisms of LV PFC emissions in recent years and no correlation has been found between HV emissions and LV emissions. LV PFCs may be emitted from specific anodes or be limited to some localized areas of the reduction cell and do not develop into HV emissions. Emissions are typically at a lower rate than HV emissions and may appear to be continuous because process control software is not triggered to take mitigation action.
Cell Start Up emissions (CSU)	When new or refurbished reduction cells are brought online many operators use a procedure where the new cell is initially operated at a higher voltage than normal for a period of an hour or more to provide extra energy to bring the cell to the target operating temperature. This high voltage is mostly related to high resistance at startup but the increase in cell voltage can result in PFC emissions, referred to here as CSU emissions. Conventions differ among operators as to when voltage starts to be measured. Sometimes it is from the first moment power is applied to the cell. For other operators, voltage is recorded when the liquid bath or alumina is added to the cell, or only after a delay put in by a timer.

1.3 IPCC Methods for PFC emissions accounting

The main driver for providing updated guidance on PFC measurement was the 2019 IPCC refinement to the 2006 Guidelines for National Greenhouse Gas Inventories. The refinement describes nine different accounting methods across Tier 1, Tier 2 and Tier 3 (Figure 2). Tier 1 and Tier 2 methods are applicable by technology class and allow for accounting of PFC emissions using the latest default factors or coefficients and methodologies. These estimates are typically subject to greater uncertainty (-76% to +580%), than can be established by making site-specific measurements (typically <15%) but allow for quick and relatively easy calculation of PFC emissions based on few process parameters. Measurements provide the greatest certainty in determining PFC emissions either through the application of methods on a site-specific basis or for determining emissions directly (Tier 3). Appendix 1 includes further details about the recommended default factors and methods for calculating PFC emissions from the 2019 IPCC refinement.

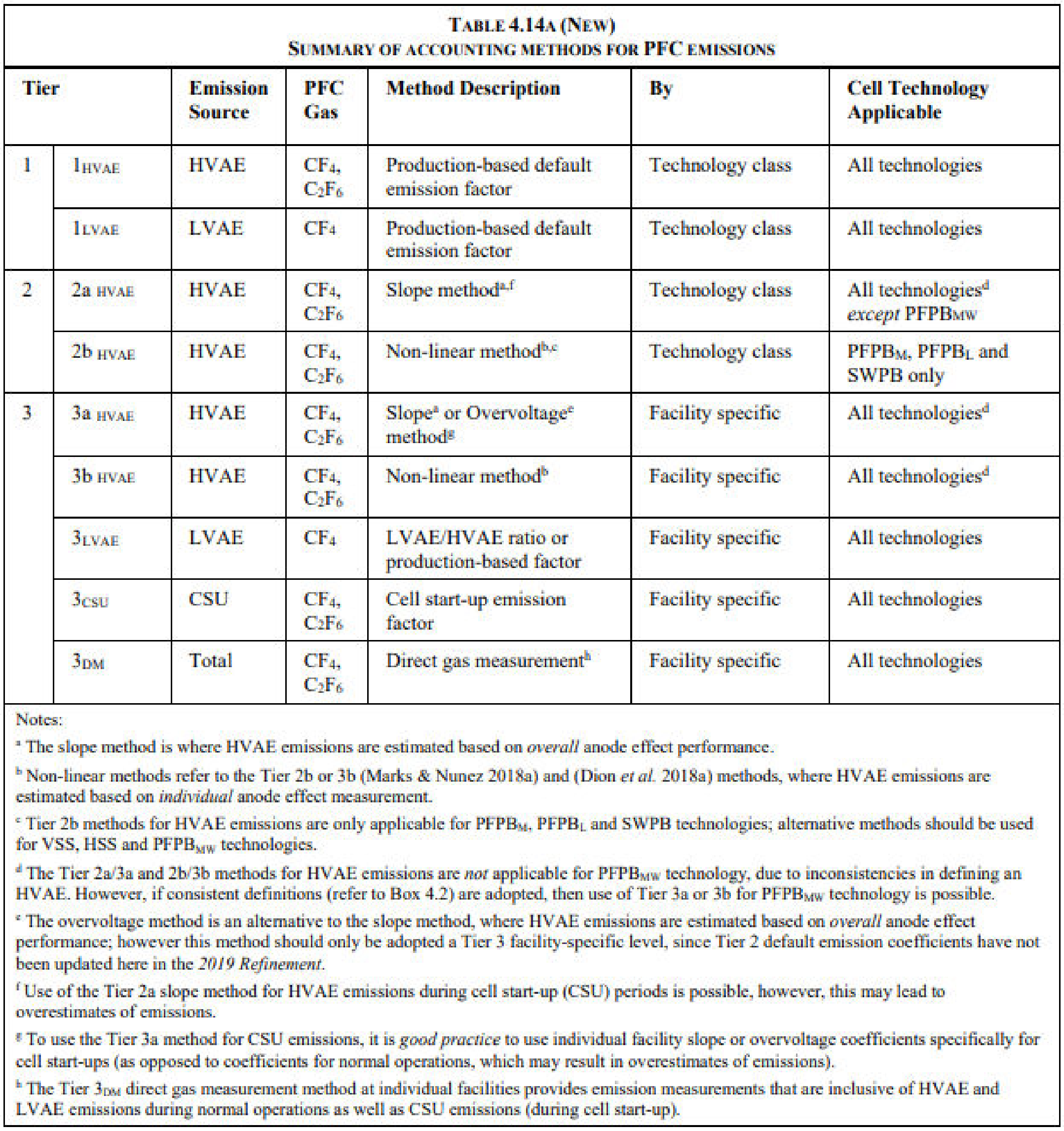

TABLE 4.14A (NEW)
SUMMARY OF ACCOUNTING METHODS FOR PFC EMISSIONS

Tier		Emission Source	PFC Gas	Method Description	By	Cell Technology Applicable
1	1_{HVAE}	HVAE	CF_4, C_2F_6	Production-based default emission factor	Technology class	All technologies
	1_{LVAE}	LVAE	CF_4	Production-based default emission factor	Technology class	All technologies
2	2a HVAE	HVAE	CF_4, C_2F_6	Slope method[a,f]	Technology class	All technologies[d] *except* $PFPB_{MW}$
	2b HVAE	HVAE	CF_4, C_2F_6	Non-linear method[b,c]	Technology class	$PFPB_M$, $PFPB_L$ and SWPB only
3	3a HVAE	HVAE	CF_4, C_2F_6	Slope[a] or Overvoltage[e] method[g]	Facility specific	All technologies[d]
	3b HVAE	HVAE	CF_4, C_2F_6	Non-linear method[b]	Facility specific	All technologies[d]
	3_{LVAE}	LVAE	CF_4	LVAE/HVAE ratio or production-based factor	Facility specific	All technologies
	3_{CSU}	CSU	CF_4, C_2F_6	Cell start-up emission factor	Facility specific	All technologies
	3_{DM}	Total	CF_4, C_2F_6	Direct gas measurement[h]	Facility specific	All technologies

Notes:

[a] The slope method is where HVAE emissions are estimated based on *overall* anode effect performance.

[b] Non-linear methods refer to the Tier 2b or 3b (Marks & Nunez 2018a) and (Dion *et al.* 2018a) methods, where HVAE emissions are estimated based on *individual* anode effect measurement.

[c] Tier 2b methods for HVAE emissions are only applicable for $PFPB_M$, $PFPB_L$ and SWPB technologies; alternative methods should be used for VSS, HSS and $PFPB_{MW}$ technologies.

[d] The Tier 2a/3a and 2b/3b methods for HVAE emissions are *not* applicable for $PFPB_{MW}$ technology, due to inconsistencies in defining an HVAE. However, if consistent definitions (refer to Box 4.2) are adopted, then use of Tier 3a or 3b for $PFPB_{MW}$ technology is possible.

[e] The overvoltage method is an alternative to the slope method, where HVAE emissions are estimated based on *overall* anode effect performance; however this method should only be adopted a Tier 3 facility-specific level, since Tier 2 default emission coefficients have not been updated here in the *2019 Refinement*.

[f] Use of the Tier 2a slope method for HVAE emissions during cell start-up (CSU) periods is possible, however, this may lead to overestimates of emissions.

[g] To use the Tier 3a method for CSU emissions, it is *good practice* to use individual facility slope or overvoltage coefficients specifically for cell start-ups (as opposed to coefficients for normal operations, which may result in overestimates of emissions).

[h] The Tier 3_{DM} direct gas measurement method at individual facilities provides emission measurements that are inclusive of HVAE and LVAE emissions during normal operations as well as CSU emissions (during cell start-up).

Figure 2: Summary of Accounting Methods for PFC Emissions (IPCC, 2019) – the focus of this guidance is on measurements related to Tier 2 and Tier 3.

2. Process data requirements – Parameters for PFC measurement planning

The following parameters should be considered when planning for and making PFC measurements at aluminum smelters.

Reduction technology	The generic reduction technology type (PFPB should be noted according to the definitions of technology types in the 2019 IPCC Methodology Report as $PFPB_{MW}$, $PFPB_L$ or $PFPB_M$). The technology type should also be further defined by specific technology, e.g., P69, A697, APxx, DX, etc. The operating line current should also be noted.
Aluminum production	The average aluminum production for the cell section measured is a key parameter because measured PFC emissions are typically normalized to aluminum production (kg CF_4 or C_2F_6/tonne Al).
Definition of high voltage anode effect	The definition of *anode effect* at the specific site should be noted. Specifically trigger voltage, whether there is any time delay before an anode effect start is recorded and whether that time delay is included in the recorded anode effect duration. The definition for the end of an anode effect should also be defined. These data are important for establishing comparability with other measurement data with similar definitions.
High voltage anode effect frequency	The frequency of anode effect occurrence (AEF) should be considered when planning the duration of the PFC measurement campaign. If average AEF is low, <0.1 anode effect per cell day, it may be difficult to obtain a statistically representative sampling of events to establish the HV emission factor with high certainty. In this case, a longer measurement period may be required.
Long term distribution of high voltage anode effect duration	A minimum record of three months of anode effect duration should be made available. Thee should represent the long-term performance of the facility. The distribution of durations of the specific anode effects measured should be statistically compared with the long-term anode effect data. The measured anode effects should reflect the long-term distribution of durations for the results to be accurate. In some cases, measurements may need to be repeated to achieve this.
High voltage anode effect start and end times for measured cells	The record of start and end times for the anode effects measured is helpful in detailed analysis of PFC emissions as a function of anode effect duration. This data is also important so that peaks in the instrument run charts that are not recorded as anode effects can be excluded from the analysis of HV emissions.
High voltage anode effect overvoltage (if applicable)	If the overvoltage coefficient is to be calculated, overvoltage for each HV anode effect measured should be made available. Some facilities have historically used the Tier 2 overvoltage method for calculating PFC emissions this methodology is no longer recommended - far more operators have used the slope method for calculating PFC emissions and it has less uncertainty. Overvoltage can however be used for Tier 3 reporting.

Notation of cell-day in operation and on any cells that are started or stopped during the measurement	The number of cells that are operating in the measurement test section is important because that determines the production of aluminum to which the measured PFC emissions will be normalized to (kg CF_4 and kg C_2F_6/tonne Al). If a cell is started during the measurements, the PFC emissions from the newly started cell should be determined separately from the ongoing operations and calculated as cell start up emissions, CSU E_{CF4} (see definitions section 1.2). An exception to this is if the Tier 2 or Tier 3 non-linear methods are used which can be applied for CSU emissions. Care should always be taken to avoid double counting emissions.
Exhaust gas flow rate at sampling point	The exhaust gas flow rate is a key parameter for the calculation of PFC emissions from PFC concentration measurements. Also, any perturbations in flow rate during the measurements is important to factor into the calculation of PFC emissions.
Net anode consumption	Net anode consumption for the measured production line should be recorded along with sulfur, inorganics and anode dust levels. This data can be used along with measured concentrations of gaseous carbon components that accompany PFC emissions as a quality control check on measured duct flow rate and as a system leak check.
Any power interruptions	During the measurements there might be either anticipated or unanticipated power interruptions, temporary power reductions or temporary increases. These events will have a substantial impact on the frequency and types of anode effects. Any power interruption events that occur during measurements should be reported and judgement exercised as to how data influenced by these events should be treated in calculating PFC emission factors. Since AEF will increase after power interruptions, we typically don't consider anode effects in the slope calculations during those periods.
Determining cell start up (CSU)	CSU emissions refer only to the initial high voltage period when the cell is cut in and does not include any longer period when the newly started cell might be subject to a higher anode effect frequency. Different operators may use different approaches to differentiate between cell start up emissions and normal operation. Most operators account for CSU separately. Care should be taken to avoid double counting in cases where CSU is not considered separately.

3. Direct Measurement Options

Different measurement approaches can be considered for measuring PFC emissions depending on the main objectives of the measurements and other considerations such as costs, equipment availability and availability of qualified personnel to conduct and analyst the measurement data.

- **Method 1:** Direct Measurement by continuous monitoring (e.g. laser) for an extended period.
- **Method 2:** Direct Measurement by real time extractive sampling (e.g. FTIR) for a limited period, typically 72 hours when AEF >0.1 AE/cell/day.
- **Method 3:** Direct Measurements of an average sample collected over a limited period (e.g. canister, bag) and projecting results to extended periods.

A combination of approaches could also be implemented to balance the needs of each site – an example of which is provided below also (Espinoza-Nava et al. 2020).

Method 1: Direct Measurement by continuous monitoring for an extended period
Background: Continuous monitoring may consist of direct installation of sensors that continuously measure the concentration of PFC components in the exhaust stream, or extractive methods, e.g. Fourier Transform Infrared Spectroscopy (FTIR) monitor). Currently, there are no reports of a proven commercial sensor in routine use for the continuous monitoring and reporting of CF_4 and C_2F_6 emissions over an extended time to meet the need for measuring the combined emissions from both HV and LV events, but research is ongoing. **Key considerations:** Candidate technologies must meet demanding requirements of high sensitivities for the PFC target gases as well as reliability. Another challenge is that the designs of aluminum smelter fume collection systems are such that there are multiple exhaust points that must be monitored for a complete facility measurement. The operation of existing extractive technologies e.g. FTIR over an extended period of time is not widely practiced due to the high cost and expertise required to operate measurement and analysis equipment. Sensors may provide an alternative solution, but many are still in a testing phase. **Equipment and systems**: The success of continuous laser monitoring systems for hydrogen fluoride (HF) is promising and implies it may be possible to develop a viable continuous PFC monitoring system. Tunable Diode Lasers (TDL) are used to monitor HF emissions but they were not deployed to PFC measurements due to hardware cost and they are less sensitive in the near-infrared region. Quantum cascade lasers (QCL), which are used in the mid-infrared region, have the potential to be used when the plant has few gas treatment centers. QCLs are generally thought to be promising technology as they won’t drift, have limited interference and have the required detection limits to measure LV emissions. Testing equipment on-site will be key to determining if such technology can be reliably implemented.

Method 2: Direct Measurement for limited time by real time extractive sampling

Background: Infrared spectrometry has most often been used to measure smelter PFCs in past measurements. Both CF_4 and C_2F_6 have strong absorbance peaks in the infrared area of the spectrum. These measurement methods have the advantage of good sensitivity and selectivity for CF_4 and C_2F_6 allowing for monitoring moment to moment assessments of concentration which, along with duct flow rates, can be used to calculate masses of the PFCs per unit of time.

Key Considerations: A major advantage in having the ability to measure CF_4 and C_2F_6 in near real time is that it enables the direct calculation of the individual emission factors for HV events, LV events and CSU for potlines already in operation. The ability to determine the HV and LV emissions factors separately and individually allows the projection of measured HV emission factors and CSU emissions into the future based on anode effect process data (see Appendix 2 for more information on differentiating between LV and HV emissions).

An important consideration with real time direct measurement is the expertise required to set the measurement equipment in place and conduct the post collection data analysis. Also, the accuracy of using the Tier 2a method of projecting emission factors depends on how well the anode effects measured represent the distribution of anode effects into the future, and, if the measured LV emission factors continue to have the same future relationship to the HV as during the measurements.

Cost is also a critical consideration especially where regulations stipulate measurements must be conducted every 36 months or when the distribution of anode effect durations has changed due to process changes. Equipment is a high cost investment and the measurement duration can extend the cost of sampling if representative anode effect performance is not obtained during the initial measurement period. There are third party companies performing PFC measurements for smelters and it is good practice to include a pre-qualification step to ensure robust procedures and quality control steps are established before a field test campaign (see Appendix 3).

Equipment and Systems: Various types of infrared measurement devices have been used for measuring PFC emissions from primary aluminum production for limited time sampling and whole facility projection (see Appendix 4).

Method 3: Direct Measurements of an average sample and post sampling analysis

Background: Collecting a representative sample of exhaust gas in a collection vessel, or, onto some sort of absorption medium and analyzing for CF_4 and C_2F_6 post collection either at the facility where the collection took place, or some other location has several potential advantages.

Key Considerations: The methodology has the potential for comprehensive facility PFC emissions assessment by placing collection vessels or media throughout the facility at all fume exhaust locations.

It typically results in all types of PFC emissions being collected together, which can be useful for total emissions sampling or reporting; however, without combining with other methods, this approach does not allow for distinguishing between HV and LV emissions which may be important for some sites or measurement campaigns. Consideration should also be given to preserving the sample during vessel retrieval and transportation to the final analysis location. For example, if gas bags are used for sample collection and air transportation is anticipated, the bags should not be filled to more than 75% capacity to account for expansion during shipping. Both gas bags and canisters should also be cleaned before use. Bags should be flushed with clean air or nitrogen before use and canisters should be cleaned according to manufacturers' recommendations.

Equipment and systems: Average samples have been previously collected by low volume rate gas sampling pumps into gas bags. Gas bags are available with capacity up to 200 liters (see Appendix 4). The sample bags have proven effective for PFC sample collection and transport by air to remote locations. The bags can be reused after evacuating them with a vacuum pump and can be cleaned by sequentially filling with high purity nitrogen and then evacuating with a vacuum pump.

Stainless steel canisters have long been used for passively collecting environmental gas samples Canisters are evacuated and then a critical orifice valve allows the environmental sample to be collected for periods from hours to a month (e.g. Fraser et al. 2013) based on the flow restrictors that have a critical orifice. Calibration of the flow is performed before the sampling and pressure gauge readings are checked to ensure the canister is being filled over the measurement time. The valve is then closed, and the canister sent to a laboratory for measurement.

Adsorption on a solid media has also been used to collect and concentrate CF_4 and C_2F_6 emissions (Bouchard et al., 2009). As with the other vessels, after sample collection the adsorbent tube is transferred to the laboratory for processing and analysis.

Example: Combination of approaches to measuring PFCs

(Espinoza-Nava et al., 2020)

A combination of approaches can also be implemented to balance the needs of each site or to cross check measurement methods.

Espinoza-Nava et al. (2020) explored the use of:

1. real time direct measurement by monitoring for a limited time (Method 2); and
2. direct measurement made on an integrated-time sampling with post analysis (Method 3).

This combination allows the simultaneous measurement using a continuous monitor like an FTIR with sampling gas bags or canisters to measure total PFC emissions. The FTIR is used to calculate the HV PFC emissions and will give trends of LV emissions changes over the measurement period. These can be correlated with pot room process activities.

The gas bags or canisters can be analyzed after the continuous sampling by the FTIR or be sent to a GC-MS laboratory to measure the total PFC emissions captured over the measurement time.

The LV emissions are calculated by subtracting from HV emissions measured by FTIR as shown in the equation below.

LV PFC emission (Method 2) = Total PFC emission (Method 3) – HV PFC emission (IPCC Calculation)

This approach also generates an estimate of LV/HV ratios daily, weekly or monthly that can facilitate direct calculations during typical process activities. These LV/HV ratios can be used as an initial approach to predict total PFC emissions.

4. Sampling Design

4.1 Design for different types of measurement

Sampling design will depend on the *type* of measurement to be implemented:

Method 1: Direct Measurement by continuous monitoring for an extended period	**Location and configuration:** It is good practice to install continuous monitors downstream from the gas treatment plant, in the exhaust chimney or duct work immediately leading to the stack. **Considerations:** Continuous monitoring measurements made upstream of the gas treatment facility may require sample stream mitigation because they contain high levels of particulate matter and corrosive HF gas for continuous monitoring. Also, gas stream non-homogeneity may lead to errors or increased uncertainty.
Method 2: Direct Measurement by real time extractive sampling **(for IPCC Tier 2 and Tier 3 Reporting)**	**Location and configuration:** The exhaust gas should be sampled downstream from the gas treatment facility and the extracted sample should be first filtered through a 15µm sintered stainless steel filter, equivalent to 800 US Mesh, on the end of a stainless steel tubing inserted through a sample port in the duct. The sample is drawn continuously out of the exhaust duct using a sampling pump or a gas eductor (a gas sampling device that uses pressurized air or N_2, Ar, process gas to produce a partial vacuum that draws the sample to the analyzer) or evacuated canister through the stainless steel sampling probe. This is then transferred through a Teflon or polyethylene sample transfer line, then through a dust filter and any needed sample stream conditioning treatment required e.g. to remove corrosive gases such as hydrogen fluoride, or potential method interferences such as water or methane. **Considerations:** Samples taken upstream from the gas treatment facility will be accompanied by a high dust level so the sintered stainless filter can be wrapped in a porous material such as gas treatment facility bag material, or, even denim fabric to remove the heavy dust load. The anode effects included in the measurement period should reflect the long-term distribution of anode effect durations. Other key process parameters that should be stable include bath chemistry, anode effect termination algorithm, percentage manual terminations, anode effect min/cell-day and cell control and feed strategy. To ensure the test period is representative of longer-term performance, a histogram of HV anode effect duration or overvoltage for the measurement period should be compared with the histogram of data for at least the previous three months. Results from events that would result in atypical operation of the line should be segregated from results from ongoing normal operations and expert judgment applied as to whether to, or how

	to, include these events in the final determination of emission factors. For example, the startup of a new cell, is a normal periodic event in the long-term operation of a potline and results for cell startups should be evaluated to determine CSU emission factors.[1]. Cells on which measurements are made should be operated using the same control algorithms for which the Tier 3 emission coefficients are to be applied. A change in the control algorithm should trigger new measurements and recalculation of Tier 3 coefficients. Such a change in algorithm will likely have a significant impact on anode effect duration distribution. Some PFPB facilities, particularly $PFPB_M$ facilities, have low anode effect frequencies (<0.1 anode effects per cell day) where slope coefficients may have to be based on a limited number of anode effects. Care must be taken to ensure that anode effect measurements are representative and limited term measurements may result in increased uncertainty in calculating HV long term emissions. For these high performing (<0.1 ae/cell day) facilities adoption of the non-linear Tier 2 methodology for calculating HV emissions is recommended and will likely give a more accurate long-term inventory result than the adoption of a Tier 3 slope coefficient based on a 72-hour measurement. Alternatively, for high performing facilities with more than one operating line, or, more than one sampling point, multiple instruments can be used to increase the number of anode effects measured, or alternatively, the measurement period could be extended as needed.
Method 2: Direct Measurement by real time extractive sampling **(on a limited number of cells e.g. process improvements)**	**Location and configuration:** Measurements may be required on a single cell or small group of cells to determine the effect of changing cell control algorithms or for other research needs. Sampling of single cells is most often conducted by extracting a sample from the cell header connection duct. This location typically has a hole in the duct for insertion of a pitot probe for the purpose of balancing the exhaust flow. A stainless-steel probe can be inserted into this opening and a gas sample pumped from this point into a gas conditioning train before entering the measurement device. **Considerations:** Sampling from this position will have high levels of dust and corrosive HF gas requiring high capacity filter devices. The gas stream at this point can be poorly mixed (Dion et al. 2016). Influence of Hooding Conditions on Gas Composition at the Duct End of an Electrolysis Cell.,. and care should be exercised in interpreting results of measurements from these sampling points.

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[1] Cell start-up procedures vary among operators. Some start-up cells using procedures that emit very little PFCs; however, the most commonly used start up procedure involves imposing an initial high voltage which does emit both CF_4 and C_2F_6. This initial high voltage is typically reduced over several hours with the resulting reduction of PFC emissions to background levels. It can be useful to measure emissions from start-up events and apply these results to emissions inventories, particularly when new production lines are established, or an extensive cell refurbishment program is undertaken (Dando et al. 2009).

Method 3: Direct Measurements of an average sample and post sampling analysis	**Location and configuration:** The sample flow can be directed to a sample container such as a vacuum canister or a gas sample bag if a time average sample is being collected. Another method involves pumping the extracted gas into a sorbent column for later desorption and measurement by GC-mass spectrometry. **Considerations:** With low flow sampling pumps, samples can be collected over periods of twelve hours or more. Vacuum canisters are capable of passive sampling for periods up to one month. Gas sample bags are available up to 200 liters capacity. It is important to ensure a stable sampling flow throughout the period with less than 5% variation. The subsequent lab analysis must be made within 72 hours for tedlar bags. Multilayer metal bonded bags have been tested up to six months without loss of PFC gases.

4.2 FTIR spectral interferences

Depending on the methodology chosen for measurement of the PFC components it may be convenient to remove interferences by pretreatment of the sample stream. Two interfering components most often encountered in infrared spectroscopy are hydrogen fluoride and water vapor.

Hydrogen fluoride contents can be several hundred ppmv in the sample stream when sampling is done in the fume duct prior to fume treatment. This concentration of hydrogen fluoride can cause corrosion of metallic or glass surfaces, as well as introducing spectral interference in some spectroscopic measurement methods. If the exhaust gas is sampled downstream from the fume treatment plant the very low hydrogen fluoride concentration is not a problem. Hydrogen fluoride can be removed from the sample stream using a trap containing activated alumina, 1/8 in balls (See Appendix 4).

Water vapor may also be an interference due to physical factors and as a potential spectral interference in FTIR measurement. The physical problem arises when the sample stream is drawn from a warm, moist exhaust stream into a measurement environment where the temperature is reduced below the dew point resulting in liquid water condensing in sample lines. Condensation is problematic for rotameters and can also harm water sensitive components of measurement systems. Water can also be a spectral interference in FTIR measurement. Removal of the water to low levels can be accomplished using a Nafion or a desiccant trap containing calcium sulfate, commercially available as Drierite. The commonly used desiccant, silica gel, should be avoided for this application because hydrogen fluoride may be a component of the sample stream and react with the silica to form silicon tetrafluoride which can act as a spectral interference in infrared measurements and may further react to leave residues on sensitive instrument optics. An alternative is to use a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer filter, commercially available as Nafion, to avoid water interference.

Methane has been reported to interfere with QCL measurements. Methane can also act as a spectral interference with low resolution FTIR measurements; however, correction algorithms are available for this interference.

4.3 Locations

Safe access should be a key criterion for all sampling operations. The sampling location should be related to an unambiguous group of reduction cells for which reliable data are available for metal production, anode effect data, and line current. Net carbon consumption data is also helpful in that gaseous carbon component concentration may be useful as a tracer to confirm that the sampling system is operating without leaks.

The preferred location for PFC sampling location is the stack downstream from the gas treatment facility. At this point, the exhaust is homogenous after passing through the fume exhaust fans and gas treatment facility. Normally, the chimney exhausting the gas treatment facility will have established sample ports and platforms accessible by stairs or ladders. The gas stream at these sampling points is dust free. Although normally low in HF content the addition of an activated alumina scrubber will remove any HF present in the gas.

If the chimney location downstream from the gas treatment facility is not accessible[2], the second choice is at the entrance of the gas treatment plant. Sample ports are typically available at this location. Duct locations should be chosen to include the maximum number of cells and still maintain concentrations of CF_4 and C_2F_6 that are above the limit of quantification of the chosen instrumentation.

4.4 Homogeneity

Flow Homogeneity Requirements

For accurate calculation of total PFC emissions, the measured concentrations of CF_4 and C_2F_6 in the collected sample must be representative of the entire cross-sectional flow in the duct where sampling takes place. Mixing must be complete in the duct at the sampling location. The stack downstream of the gas treatment facility is optimum as the gases have been well mixed having passed through the fans exhausting the duct system and some regulatory guidelines specify the exact sampling locations. When this sampling location is not available, care must be exercised to avoid errors due to incomplete mixing.

Evaluating Homogeneity of Duct Flows

Potroom fume collection systems are typically designed to draw fumes from each cell into a larger duct that then merges into even larger ducts that lead to the gas treatment facility. Experience has shown that gas flows may remain segregated for some 10 meters or more after merging. The impact of this effect is that the concentration of PFC components may be quite different across the cross-sectional area of the duct. If a point sample is taken in a non-homogenous gas and the measured concentrations are applied to the full flow in the duct, non-representative emission concentration will be used in the calculation. To evaluate the impact of such errors the homogeneity of the gas stream should be evaluated across the duct cross section.

Testing for Homogeneity

Homogeneity of the gas stream at duct sampling points upstream of the fume treatment facility can be evaluated by injecting a small constant flow of a tracer gas into the exhaust duct of one of

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[2] In some installations the fume treatment facilities have multiple chimneys and the gas exiting these chimneys cannot be associated with any specific group of reduction cells. In some other facilities there may not be sampling ports available on the chimney and in some locations, there is no ladder to give access to the chimney.

the reduction cells and then measuring the variation in concentration of the tracer across the cross section of the duct at the chosen sampling point. The specific tracer gas compound and injected tracer concentration should be chosen with consideration of the measurement instrument in mind. Sulfur hexafluoride (SF_6) has been used as a tracer because it has good sensitivity for infrared measurements, is not normally present in the gas stream, and is stable at the temperature encountered in the fume duct system. However, SF_6 is also a strong greenhouse gas with a long atmospheric lifetime, its use is usually required to be reported as part of GHG inventories and should be avoided if another tracer can be successfully used.

An alternate approach is to inject a constant flow of tracer gas into the header connection ducts of cells that represent the greatest possibility for segregation and measure recovery of the tracer concentrations at a fixed sampling point.

Haloflurocarbon, R134a, commonly available as a refrigerant gas has been used as a tracer gas; however, the most commonly available refrigerant is impure. It should be noted that although very minor amounts of Halofluorocarbon may be used as a tracer gas, there may be a requirement to include it in GHG reporting. Sites should refer to their specific regulatory requirements.

Testing is not necessary if the sample is collected at the optimum location (downstream of the gas treatment facility) but can be conducted as part of a quality check procedure to ensure no leakage and accurate measurement of flow rate.

4.5 Sampling Time

Sampling should include all the normal cycles of smelter operation (i.e. tapping, tracking, feeding and anode changing). Repeat samplings may be useful to reduce uncertainty in establishing an initial baseline when LV PFC emissions are variable from one measurement period to another.

The sampling strategy should allow for a good statistical sampling representative of both of HV and LV PFC emissions. PFC emissions rates, mass per second of anode effect, vary greatly with the duration of the anode effect. Longer HVAEs have much lower emission rates than shorter HVAEs. Also, anode effects of similar duration have high variability in emissions of CF_4 and C_2F_6. For these reasons the sampling strategy should be planned to give a robust average value of the emission factor by reflecting all aspects of the aluminum production process. If possible, it is desirable to include one or more cell start-ups during the measurement so cell start up emissions can be evaluated during the measurement campaign.

For direct measurement by real time extractive sampling (Method 2), a running average for CF_4 and C_2F_6 emission factors should be calculated periodically, for example after each twelve-hour sampling period. Sampling should continue until the running average of the PFC component emission factors does not change by more than 10 percent from the previous average value. In any case, sampling and measurement should be made for a minimum of 72 hours[3] but longer

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[3] For the most modern smelters with recorded anode effect frequencies < 0.1 anode effects per cell-day, the 10 percent variability standard may be difficult to achieve, and a long-term sampling campaign may be necessary. For these facilities it is important to evaluate and report the uncertainty in PFC emission factors and the calculated Tier 3 CF_4 slope and C_2F_6/CF_4 weight ratio coefficients. The application of the non-linear method will provide a more accurate inventory than measurement of a limited number of AEs that may not be representative of longer-term anode effect duration distribution.

may be required in order to get a long-term, representative sample, especially if the anode effect frequency is low.[4]

4.6 Chimney or Duct Flow Rate

Attention should be given to proper measurement of gas flow rates in which PFC concentrations are being measured. This information is important for the proper conversion of measured PFC concentrations into emission rates. Most modern smelters have continuous monitoring data available for chimney exhaust flow to apply to PFC concentration measurements. Calibration of this equipment must be checked by location staff regularly to be sure of the flow result. Duct flow rate at the sampling point should be measured with a pitot probe (for example: EPA Method 1 – Sample and Velocity Traverses for Stationary Sources or other country reference methods) if this data is not available.

Another approach to check flow rate is by injecting a known amount of a tracer gas, e.g. SF_6, upstream of the sampling point and measuring the dilution of the tracer at the sampling point[5]. Any lack of total mixing of the tracer gas will result in uncertainty in the calculated result and should be accounted for in the overall uncertainty determination.

Duct flow rate (L/min at 0 °C and 1 atm) = I × 10^3/°C

Where:

I = Tracer injection rate (mL/min @ 0 °C and 1 atm)

C = Measured tracer concentration at sampling point (ppmv or µL tracer per liter exhaust flow)

As a final check, facility data for net carbon consumption for the test cells can be used to calculate flow rate by measuring the carbon components, mainly carbon dioxide and carbon monoxide and calculating the dilution of these carbon components after accounting for impurities in the anode carbon and atmospheric background carbon dioxide levels.

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[4] Normal smelter operations involve repeating several operational steps during which cells are tapped, fed with alumina and carbon anodes are changed on a specific schedule. Finally, there is a period when cells are allowed to electrolyze the available alumina without new additions to confirm whether the resistance is decreasing or increasing over time (“tracking”). Sampling should weight all the operational cycles as they normally occur during production. While there are no definitive studies of how LV emissions might systematically vary with the operational cycles, such an association may well exist and add additional weight to proper reflection of all phases of operation.

[5] One method that has proven accurate and easy to use in the field for injection of low flow rates of a tracer gas is the use of the Mesa Labs DryCal flow calibrator (see Appendix 3). The tracer should be injected for a period of time necessary for the measured concentration to stabilize, usually about five minutes. Knowing the flow rate of the tracer gas into the exhaust system and the measured concentration of the tracer at the sampling point the duct flow rate can be directly calculated from the dilution of the tracer gas.

5. Concentration Measurement

The accurate measurement of the concentration of the two PFC components along with the simultaneous assessment of duct flow rate at the sampling point is required to calculate PFC emission factors.

5.1 Calibration standards

Standards should be procured for CF_4 and C_2F_6 that cover the range of expected concentrations to be measured for LV, HV and CSU emissions. LV CF_4 concentration at the chimney measurement location normally range from 0.01 ppmv up to 1 ppmv. During HVAE anode effects at the same location CF_4 concentration rapidly rises to levels of 0.5 to 10 ppmv. It is desirable to design sampling to keep measurements within the instrumentation linear range. If, however, concentrations are encountered outside the linear range the instrument should be calibrated with standards that accurately reflect the non-linearity.

C_2F_6, if detectable, can be expected to be present at about 5 to 10 % of the CF_4 volumetric concentration and standards should reflect these expected ranges. C_2F_6 has not typically been observed as part of LV PFC emissions.

Commercial standards obtained from gas suppliers are normally prepared by gravimetric means and "certified" to 5% accuracy. These standards are adequate for most purposes; however, certification by a nationally recognized standards body such as NIST in the US, or a comparable source from another country, is desirable to reduce uncertainty due to calibrations.

In addition to the two target PFC components, working standards may be required for gaseous compounds that typically accompany the PFCs in the smelter exhaust. Typical concentration ranges found in the smelter exhaust are shown in the table below.

Table 1 - Typical Composition of Smelter Exhaust Duct Emissions (based on expert opinion, Marks 2020)

Component	Concentration
Carbon dioxide (CO_2)	0.6 – 1.2 vol %
Carbon monoxide (CO)	0.04 – 0.12 vol %
Water (H_2O)	0.01 – 2.5 vol %
Sulfur dioxide (SO_2)	0 – 0.08 vol %
Carbonyl sulfide (COS)	0 – 0.05 vol %
Hydrogen fluoride (HF)	0 – 0.25 vol %
Methane	0.0002 – 0.0004 vol %

Some measurement methods, such as low resolution FTIR require software corrections for overlapping spectral components. Accurate measurements at the lowest PFC concentrations require good standards of accompanying gas components. If a tracer gas is to be used to check for sampling system integrity or to calculate duct volume flow rate additional standards may be required. Sulfur hexafluoride (SF_6) has been successfully used as a tracer gas at concentrations of 0.5 ppmv to 1 ppmv. Due to sulfur hexafluoride's high GWP another commonly available gas, R-134a (1,1,1,2-Tetrafluoroethane, $C_2H_2F_4$), has been used as a tracer gas.

SF_6 tracer is used as commercial grade, typical 98% or higher. The 0.1 to 1 ppm are the concentration that are typical measured by the instrument after dilution.

Secondary working standards can be made by diluting a certified standard using a gas dilutor device. Care should be exercised when using these devices for preparation of standards at fractions of a ppmv. These dilutions should be carefully tested for linearity to assure validity before use in a calibration procedure.

6. Measurement Procedures, Calculations and Reporting

6.1 Method 1: Direct Measurement by continuous monitoring for an extended period

On-line measurements – such as QCL or tunable diode laser absorption sensors (TDLAS) – are defined as those that are placed directly in the exhaust stream and continuously record the concentration of the PFC compounds. These approaches offer the potential for recording total PFC emissions continuously over extended periods of time. This avoids the need to project emission factors based on anode effect process data, which tends to introduce uncertainty to the inventories. This uncertainty comes from changes in the Slope value with changing anode effect duration distribution.

If LV emissions are to be measured continuously along with HV emissions the detection limit of the device must be at least 0.01 ppmv. In order to ensure such limits are achievable, existing references can be referred to e.g. ASTM method D6348 "*Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy*" and/or EPA method 320 "*Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy*". The measurement instrument should also be capable of measuring transient signals of less than one second at concentrations up to 10 ppmv that exist in some instances such as during long anode effects, overlapping anode effects, or, cell start-ups. The instrument's response signal must account for differences between calibration and measurement gas temperature and pressure for an accurate concentration output.

6.2 Method 2: Direct Measurement by real time extractive sampling for a limited time

At-line measurement approaches involve calculating PFC emission factors based on at line continuous measurements for a defined sampling period and has been the most often used approach for aluminum smelters to date. In this approach, a small sample of the exhaust stream is drawn by pump or gas eductor into the measurement device where the concentrations of the target compounds are recorded. Sampling is configured as a continuous flow through cell where the sample is analyzed. In any case, it is important that the instrument and sampling approach be capable of fast response because for HV events for pots in operation or a CSU, the PFC concentrations change at very fast rates. Appendix 5 provides further information on sampling and instrumentation and calculating emission factors based on at line instruments continuously measuring duct PFC concentrations.

As above, if LV emissions are to be measured the detection limit of the device must be at least 0.01 ppmv. Existing references can be referred in order to achieve such detection limits to e.g. ASTM method D6347 or EPA method 320.

6.3 Method 3: Direct Measurements of an average sample and post sampling analysis

Emission factors determined by sampling into canisters, bags or sorbent columns are by nature total emissions, and, possibly include CSU emissions if cells were started during the sampling period. This approach offers the potential for the most comprehensive assessment for PFC emissions facility wide as sampling can be conducted at each exhaust chimney. Appendix 6 has further information on calculating emission factors based on sampling into bags or onto sorbent

Columns for measurement. This comprehensive measurement does not distinguish among LV, HV or CSU emissions.

6.4 Combining methods to calculate different emissions factors

For some facilities that operate with low anode effect frequency it may be possible to determine LV emissions by selectively choosing sampling periods during which there are no HV events. Other sampling periods that have HV events can then be used to calculate the HV emission factor by difference.

HV PFC emissions = total – LV PFC emissions

and

LV PFC emissions = total – HV PFC emissions

The HV CF_4 and C_2F_6 emission factors can then be used to calculate facility specific Tier 3 Slope and Ratio coefficients. These coefficients can then be applied to facility anode effect process data to calculate total HV related emissions.

The CF_4 and C_2F_6 emission factors for CSU could be measured in a similar way by sampling during a period with a CSU to measure the total emissions for the period, HV, LV and CSU emissions and the CSU could be calculated as the difference between normal total emissions and total emissions including the CSU. It is also possible to use Tier 2b or Tier 3b approaches to evaluate the CSU factor, with the CSU polarization time, the time the cell exceeds target operating voltage, as the variable to build the factor.

6.5 Linear and Non-Linear Methods for HV emissions

Tier 2 and 3 linear method (tier 2a and 3a): adopt a linear model that predicts a linear increase in CF_4 emissions with a linear increase in the anode effect minutes. Tier 2a method is based on the average of slope factors from a database of prior measurements on defined categories of reduction technologies. Tier 3a is the calculation of a facility specific slope factor from measurements at the facility. Measurement data for CF_4 emissions from individual anode effects show that CF_4 emission rate (kg CF_4/AE min) is highest from shortest anode effects and drops precipitously for longer anode effects (see Appendix 7). Changes in anode effect duration distribution has been the factor identified as the cause where there have been changes in slope values noted from repeat measurements at specific facilities.

Tier 2 non-linear method (tier 2b): a non-linear approach has the potential to be a more robust calculation not affected by changes in distribution of anode effect durations. Models have been developed (Marks & Nunez, 2018, Dion et al. 2018a) to predict emissions for individual anode effects based on the available data relating individual anode effect CF_4 emissions, anode effect duration and metal production rates. Comprehensive adoption of the non-linear method would require facilities to calculate emissions from each individual anode effect using the model equations to construct an inventory. This approach would require facilities to adapt existing software to incorporate the calculation into the anode effect recording program.

Tier 3 non-linear method (tier 3b). A tier 3b approach develops a non-linear predictive model based on the facility specific measurement. To date this approach has not been extensively investigated as an alternative to the slope method but has the highest potential for improving the HV PFC emissions inventories.

In order to develop a tier 3 non-linear approach access to the individual anode effect parameters (duration, energy, exact starting time, etc.) that are monitored for HV PFC emissions is required. In parallel, individual calculations of the CF_4/C_2F_6 emissions can be perform on all individual AE using a integration law (such as trapezoid or Simpson's 1/3). Using the collected dataset, it is possible to create a database of individual AE in order to reproduce a similar methodology to the literature to develop smelter-specific coefficients for the non-linear equations.

This methodology has good potential in facilities with a higher HV AE frequency as a reasonable amount of individual AE can be monitored within a week or two. The available range of the AE duration distribution will have an impact on the strength of the correlation. Therefore, an extensive range of AE duration should be aimed for while collecting the data.

Finally, overlapping AE may add difficulties in establishing the individual AE database properly. Such occurrences should be rejected if they are less than 20% of the total events. On the other hand, it is possible to use a more complex methodology (Dion et al. 2018a) with optimization functions to decompose the respective emissions amount of gas emitted during each individual anode effect.

6.6 Total Emissions Reporting

Total emissions reporting for PFCs includes emissions from HV events, LV emissions and CSU emissions[6]. Total emissions can be calculated using a variety of approaches which are outlined in this section.

$$Total\ E_{CF4} = (HV\ E_{\mathrm{CF4}} + LV\ E_{CF4} + CSU\ E_{CF4})$$

$$Total\ E_{C2F6} = HV\ E_{C2F6} + CSU\ E_{C2F6}$$

Where:

Total E_{CF4} = Total CF_4 from aluminium production, kg CF_4

Total E_{C2F6} = Total C_2F_6 from aluminium production, kg C_2F_6

HV E_{CF4} = HV emissions of CF_4 from aluminium production, kg CF_4

HV E_{C2F6} = HV emissions of C_2F_6 from aluminium production, kg C_2F_6

LV E_{CF4} = LV emissions of CF_4 from aluminium production, kg CF_4

CSU E_{CF4} = CSU emissions of CF_4 from aluminium production, kg CF_4

CSU E_{C2F6}= CSU emissions of C_2F_6 from aluminium production, kg C_2F_6

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[6] Some operators use cell start up procedures that do not release measurable PFC emissions. Also, some operators account for cell start up emissions within the slope calculation by integrating cell start up high voltage time into total anode effect minutes along with measured PFC emission rate.

Method 1: Direct continuous measurements for an extended period

Direct continuous measurement approaches give the total of all the emission sources with no need to differentiate the different types of emissions. This approach is recommended if technology is available and it is economically feasible to apply on an ongoing basis to an entire facility. The candidate measurement method must be shown to have a minimum detection limit for CF_4 of 0.01ppmv to be considered for LV CF_4 measurements. Calibration confirmations should be carried out to by comparison of the measurement method results to results obtained with a proven alternate measurement technique. Also, recovery tests by periodic injection of the target compounds or suitable surrogates are useful to demonstrate method efficacy.

Determining total emissions by IPCC Tier 2a Method

The following steps should be followed when PFC inventories are constructed based on the IPCC Tier 2a method which relate facility process anode effect data to emissions.

HV: Calculate HV E_{CF4} by multiplying the technology specific slope coefficient by the average anode effect minutes per cell day for the inventory period.

Calculate HV E_{C2F6} by multiplying HV E_{CF4} by the appropriate technology specific ratio ($R_{C2F6/CF4}$).

LV: Calculate LV E_{CF4} using Tier 1 or Tier 3 methods.

CSU: There is no Tier 2 method for determining CSU emissions, but these can be estimated as HV events by applying the appropriate non-linear equation to the HV time recorded for the cell start up. The Tier 2a methodology could also be used but may provide an overestimate of CSU emissions.

Determining total emissions by IPCC Tier 3a Method

Application of the Tier 3 slope or overvoltage method requires making measurements of PFC emissions at the facility. The measurements must be capable of differentiating HV and LV PFC emissions in order to calculate the Tier 3 slope factor. Guidelines for differentiating the two types of emissions are noted in Appendix 2.

HV: Calculate total HV CF_4 by analysing the measurement data (see Appendix 2).

Calculate the total anode effect minutes for the measured cells for the measurement period from facility anode effect process data.

Calculate the total tonnes of aluminum produced by the cells during the measurement period.

Calculate the slope factor or the overvoltage factor from the data, as the average kg HV CF_4 per tonne aluminum produced divided by the average anode effect minutes per cell day (see Appendix 5, step 4 for continuous measurements or Appendix 6, steps 7 and 8 for consolidated samples).

Calculate the facility specific weight ratio of C_2F_6 emissions to CF_4 emissions, $R_{C2F6/CF4}$, from the measurement data.

LV: Calculate LV CF4 emissions by subtracting HV CF4 from total measured CF_4.

$$LV\ CF_4 = Total\ CF_4 - HV\ CF_4$$

Determine facility specific ratio of LV/HV CF_4 emissions as described in Appendix 2.

CSU: In order to include CSU emissions in the Tier 3 inventory process, ideally five or more CSUs should be measured, and emissions recorded. This many CSUs in a single measurement campaign is rare and previous measurements could be used if start up procedures are comparable.

Calculate the kg CF_4 per start up high voltage minute or define the slope or overvoltage coefficients.

These events are long lasting compared to anode effect duration and are difficult to capture isolated from normal anode effect events that overlap the time period in which the startup occurs (Dando et al. 2009).

Calculate any emissions from overlapping anode effects from other cells in the measurement group. Estimates can be made by constructing a plot of CF_4 emissions vs anode effect duration for isolated anode effect events. Methods have also been described to deconvolute emissions from overlapping anode effects (Dion et al. 2017).

Calculate CSU $R_{C2F6/CF4}$ - this is expected to be lower than for normal anode effects because C_2F_6 emissions cease before CF_4 emissions stop.

Subtract the anode effect CF_4 and C_2F_6 from the total measured CF_4 and C_2F_6 to ensure only CSU emissions are recorded.

When measurements are not available the Tier 2 non-linear method applied to the CSU high voltage time is the best alternative for estimating CSU emissions.

6.7 Data processing

Measured parameters (HV, LV and CSU emissions E_{CF4}, E_{C2F6}) should be reported along with calculated uncertainty or estimated uncertainty using expert judgement. The data points required to construct site wide inventories is outlined below for different methodologies.

On-going complete facility monitoring

When a comprehensive site wide monitoring system is in place total PFC emissions are the direct product of the measurement process and the site wide inventory is a direct result of the on-going measurements.

Inventory by slope or overvoltage method

Detailed equations for calculating Tier 3 CF_4 slope or overvoltage factors and C_2F_6 ratio coefficient, $R_{C2F6/CF4}$ are described in Appendix 5 (Method 2) and Appendix 6 (Method 3).

Measurement data should be analyzed to calculate HV CF_4 emissions separately from LV CF_4 emissions (Appendix 2). A Tier 3 slope coefficient is then calculated from the HV emission factor, E_{CF4}, as the ratio of E_{CF4} to average anode effect minutes per cell day.

The LV/HV ratio is calculated (Appendix 2) and LV E_{CF4} is calculated by multiplying this ratio by the HV E_{CF4}.

Total PFC emissions for a potline inventory period, typically one month, is then calculated by summing:

a) the HV CF_4, calculated from the slope coefficient times the average anode effect minutes per cell day times the tonnes aluminum production for the period,
b) plus, the LVAE CF_4, calculated by multiplying the LVAE/HVAE CF_4 ratio times the HVAE CF_4.
c) emissions of C_2F_6 are calculated by multiplying the $R_{C2F6/CF4}$ times the calculated amount of HV CF4 for the period.

Inventory by non-linear equation method

To construct an inventory by the non-linear equation method the HV emissions are calculated for each recorded HV according to either the Tier 2 non-linear equations proposed by Nunez and Marks (2018) or Dion et al. (2018a) or, by a Tier 3 approach where a non-linear equation to fit measurement data for the specific facility. For each anode effect recorded the kg CF_4 is calculated from the non-linear equation during the inventory period. The LV/HV ratio is then applied to calculate LV emissions.

7. Quality

7.1 Measurement systems (leaks, recovery, calibration)

Instruments used for PFC measurements should be calibrated with reliable standards, preferably certified by a recognized standards body, and have demonstrated capability for making measurements of CF_4 and C_2F_6 for the expected concentrations.

Gas transfer tubing and connections to the measurement system should be checked for leaks prior to beginning sampling. Checks should be made to make ensure all tubing and systems are airtight. If no leak is detected, sampling can start. If an unacceptable leak is detected (> 0.02 m^3 / h. At 51 kPa or 2% of the normal sampling rate), the leak should be located and mitigated.

Throughout the measurements there should be regular checks on duct flow rates and any deviation should be reflected in the translation of concentration measurements into PFC emissions. Leak checks and accurate flow monitoring are especially important for Method 3.

In addition to conducting a leak rate test on the evacuated sample transfer system, measurement of carbon species in the gas sample is a good confirmation of a leak free system.

Recovery tests should be performed by injecting a tracer gas into the duct system and measuring recovery. Sulfur hexafluoride injection has been successfully used as a tracer as has R134a. Another useful recovery test that should be utilized when measurements are made with FTIR instrumentation is to measure the carbon components, primarily carbon dioxide and carbon monoxide, in the exhaust gas and, after correcting for background atmospheric carbon dioxide, compare with expected total gaseous carbon levels based on the facility's net carbon consumption process data.

7.2 Competence requirements

Obtaining reliable PFC measurement results require both competence in the measurement methodology and knowledge of the smelting technology being measured. This combined competence can be met through close coordination between smelter technical staff and measurement experts if both areas of expertise are not available in measurement staff.

Initial capability can be assessed by sending standards of known composition or samples that have previously been analyzed to candidate laboratories for measurement.

7.3 Data checks

Measured parameters should be checked against the data in Appendix 1, which contains average values and uncertainty ranges calculated from measurements made in many facilities. If the measured parameter is outside the limits of uncertainty noted in the Appendix 1 the data should be reviewed for errors.

If the measurement is made for a limited time and is to be projected to calculate future emissions the distribution of anode effect durations should be compared with the long-term anode effect duration distribution. The data should be carefully checked for comparability of extended duration anode effects, those with duration exceeding 100 seconds. One or more of these long anode effects, particularly those anode effects requiring manual intervention which can have durations of several hundred seconds, can skew the average for anode effect minutes per cell day, the denominator in the slope equation. The contribution of long anode effects in the measurement period should reflect the long-term distribution of long anode effects.

Smelter operations during the measurement period should be reviewed with location technical staff to be sure that there were no operations during the measurements that would not be representative of the long term. Any interruptions, such as short-term fan shutdowns for maintenance, in the fume capture fan system should be identified. In some instances, adjustments to the data can be made when short term flow disturbances are encountered by correcting measured PFC concentrations based on carbon dioxide or carbon monoxide concentrations.

The non-linear Tier 2 equation can also be used to give an approximate check of total PFC emissions for the measured HV.

7.4 Uncertainty

An important element of reporting PFC emissions in any measurement procedure is to report the uncertainty of the reported emissions. General guidelines for assessing uncertainty are documented in the 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.

A detailed list of sources of uncertainty should be developed. All efforts should be made to eliminate or minimize sources of uncertainty; however, all measurements have residual uncertainty and the best estimate of the uncertainty of each source should be noted. The combined impact of all the sources of uncertainty should be reported along with any report of emission factor or total PFC emissions.

Examples of some sources of uncertainty include:

a) measurement instrument calibration and standards uncertainty
b) uncertainty in analytical measurement software
c) impact of interferences,
d) uncertainty in chimney or duct flow rates
e) homogeneity of sample stream

8. Safety

It is of paramount importance that all safety practices of the smelter where the sampling is carried out are strictly complied with. Most production sites require on-site safety training and strict compliance with location-specific safety rules. Prior to starting sampling work a pre-task and a job safety assessment should be conducted with all the stakeholders, including maintenance, potline, and environment staff. These assessments should make reference to safety procedure of the site. There are numerous safety hazards in primary aluminum smelters, and it is important to consider the hazards and risks that may arise during PFC measurements and take steps to mitigate them. For the most part, those engaged in measurement of PFC emissions will not be required to work inside potrooms unless a process development objective requires working there. In some measurements, in order to assess recovery, or, for homogeneity tests, there will be a need to inject the tracer gas inside the potroom. Smelters have rules with respect to use of compressed gases in potrooms and location staff should be available to assist with this operation. Also, there is often a requirement to pass through one or more potrooms to reach duct or chimney sampling areas.

8.1 Personal Protective Equipment (PPE)

An approved hard hat, safety glasses and steel toe safety shoes are essential PPE equipment that is required to enter most smelter facilities. Some operators require wearing fume protection masks while transiting through potrooms on the way to sampling sites outside the potroom. Flame retardant clothing is required for any work inside the potroom and some operators require this be always worn in the facility. Hand safety is important for all operators and wearing the proper gloves for the activity is required. Hearing protection should always be part of the worker PPE. In many instances sampling points are in high noise level areas resulting from fume exhaust fans, air blasts to and vibration equipment to move alumina. Measurement staff should consult specific on-site protocols to ensure suitable PPE is used.

8.2 Hazards

Specific hazards which may be encountered while making measurements inside the aluminum smelter will be identified during the initial safety orientation. Typical hazards encountered include:

a) Plant vehicle traffic. In most cases plant work vehicles have the right of way. It's important to keep a watchful eye, stay on marked walkways, use proper pedestrian entries and exits, and give way to any inside vehicle.
b) Overhead cranes move through the potrooms.
c) Falling objects. Work in smelters takes place on many different elevated areas and tools or parts can easily escape and fall to the ground.
d) Corrosive and noxious fumes. Hydrogen fluoride (HF), sulfur dioxide (SO_2) and ultrafine particulates (PM_{10} and $PM_{2.5}$) can be encountered during some work operations inside the potroom, or from fume collection ducts prior to fume treatment.
e) Electrical shock hazards. High voltages are common inside potrooms and untrained personnel should always be accompanied by location staff while working inside the potroom.
f) Pinch points. This may result from heavy equipment on feet or hands.

g) High noise levels.
h) Hand cuts and abrasions.
i) Hot material splashes and/or hot surfaces.
j) Liquid aluminum in cells can result in explosion with water contact.
k) If working at heights off ground proper harnesses should be used to protect against falls.

9. Measurement Frequency and New Measurements

For many smelters it is good practice to repeat measurements for HV emissions every 36 months or if there has been a significant process change. Some jurisdictions will have minimum frequency requirements outlined in regulation. Local and regional regulatory guidelines for measurement frequency should be complied with. Significant process change refers to changes such as changes in the anode frame, and changes to the pot control algorithm, line amperage increases greater than 10%, and, significant changes in the anode effect duration distribution.

The major factor affecting the relationship between anode effect minutes per cell day and aluminum production normalized CF_4 and C_2F_6 factors for HV emissions is the distribution of anode effect durations which include AE manually or automatically killed. The distribution of anode effect durations is particularly impacted by longer anode effects (particularly those associated with manual anode effect kills >100 seconds). Changes in the distribution change the slope factor. A higher proportion of longer anode effects lower the slope factor, while eliminating longer anode effects increases the slope factor. A recommended test for the impact of changes in anode effect duration distribution is to apply the Tier 2 or Tier 3 methods or if available, non-linear equation to the anode effect duration data. If the result varies by more than 15% (normal expected uncertainty for establishing the IPCC slope coefficient), then a new measurement should be considered (Dubois et al. 2019).

Data is not currently available to predict the consistency of LV emissions over time for individual potlines. For legacy technology operators, including $PFPB_L$, SWPB, VSS and HSS operators, LV emissions make up a minor fraction of the total PFC emissions and expected changes in LV emissions should not significantly affect total PFC emissions over a limited period of 36 months for example.

LV emissions can account for a significant amount of the CF_4 emissions for large, modern technology cells ($PFPB_M$ and $PFPB_{MW}$) (Li et al. 2012, Batista et al. 2018). Measurements made over a period of 72 hours show that these emissions are highly variable, however data is not available to predict longer term variability of average LV emission factors. The growing awareness among operators of the contribution of the LV emissions is driving process changes to lower these emissions. If on-going continuous measurements are not in place at these modern technology smelters, periodic collection of average bag or canister samples to test for consistency of emissions should be collected to develop confidence in the long-term average total PFC emissions.

10. Future Options for Process Modelling of LV emissions

As described previously in the document, LV PFC emissions are relatively new and difficult to study extensively under industrial conditions, particularly due to the cost of measurement, the very low gas concentrations, and erratic emissions from multiple sources. All these make it difficult, at the present time, to develop an accurate estimation model to properly account for LV PFC emissions. Nonetheless, future work in the field will inherently add important knowledge to this area and may eventually allow the development of improved methodologies to estimate LV emissions, using process signals.

Based on the current literature, the most promising technology that could eventually lead to a reliable modelling of this type of emissions is related to continuous anode current monitoring. Limiting its use today is the low uptake of the technology across entire smelter potlines. However, numerous studies (Cheung, Cheug Y., 2013; Dion L., et al. 2017; Yao, Y., Bao, J., Skyllas-Kazacos, M. et al. 2018; Yang, S., Zhang, H., Zou, Z. et al. 2020; Wong, D.S. & Welch B. 2018; Dion et al. 2018; Kolas, S., et al. 2015) in the last decade have shown that this specific type of measurement offers the potential to detect the “near-exact” moment when, and precise location where, PFC emissions start to be produced in an aluminum reduction cell. Up to now, such detections are mostly used in order to acquire knowledge on LV emissions, improve process behavior or launch preventive AE treatment sequences in order to rapidly eliminate emissions.

Some of these studies (Yang, S., Zhang, H., Zou, Z. et al. 2020; Wong, D.S. & Welch B. 2018; Dion et al. 2018; Kolas, S., et al. 2015) looked at simultaneously relating data from anode current signals with corresponding measured PFC emissions. Most of these focused exclusively on binary correlations (PFC levels detected vs not detected) between both signals, with promising binary outputs. However, one study (Dion, L., et al. 2016) explored the use of neural networks leading to successful qualitative and quantitative estimates of PFC emission intensities (Figure 3). This demonstrated that with the correct input variables, it is possible to predict or estimate LV emissions with some accuracy. However, the current model proposed is rather complex and unfit for widespread industrial use.

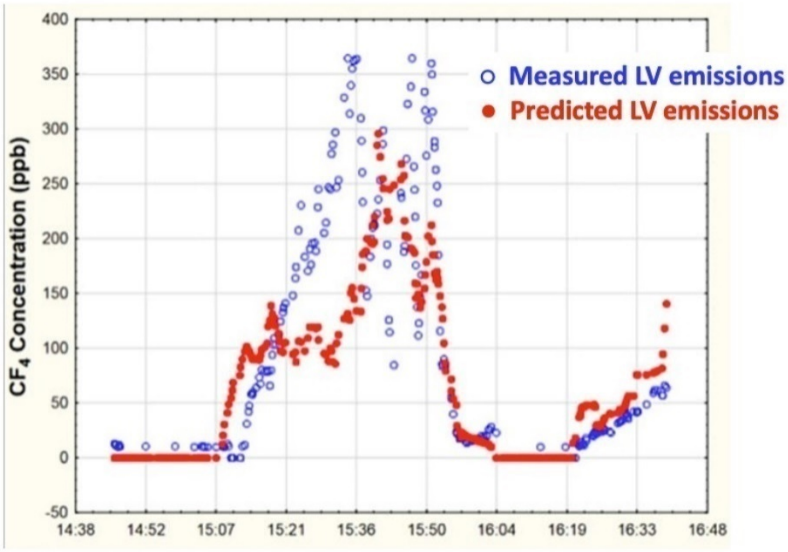

Figure 3: Example of measured (blue) low voltage CF4 emissions vs. predicted emissions (red) using models based on anode current data (Dion et al. 2016).

A recent paper (Boulanger, J., et al. 2020) observed three characteristic anode current signatures during low-voltage PFC emissions. Such work could pave the way to properly associate the deviation of current intensities and their duration to the magnitude of LV PFC emissions. Thus, a proper use of these new variables could be relevant to develop more accurate estimation model for LV PFC emissions.

Other than individual current monitoring, some researchers have highlighted that improvements or updates to existing equipment can provide the necessary information to detect the occurrence of PFC generation in an electrolysis cell. Some examples of beneficial improvements that could benefit LV detection and quantification are: smart feeders (Hvidsten, R. & Rye, K.A. 2007), improved sensitivity and proper usage of the cell voltage signal (Wong, D.S. & Welch B. 2018; Batista, E. et al. 2016), high frequency analysis (Cheung, Cheug Y. 2013; Kolas, S. et al. 2015) and principal component analysis (PCA) (Yao, Y., Bao, J., Skyllas-Kazacos, M. et al 2018). Until now, these studies did not attempt to quantify the intensity of the emissions with such tools or indicators.

In conclusion, the current state of the art reveals that precise quantification of LV PFC emissions is a difficult challenge. While there is currently no clear methodology that can estimate LV PFC emissions based on process parameters, it is likely that such model will be developed as knowledge on this topic and smelter technologies evolve with time. Finally, the widespread use of Industry 4.0 technologies will certainly offer great opportunities to efficiently process the very significant amount of data collected by facilities. This will likely play a major role in establishing correlations between a smelter's numerous process variables (cell voltage, alumina concentration, anode currents) and LV PFC emissions.

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APPENDICES

Appendix 1 - Recommended Tier 1 and Tier 2 Factors for Calculating E_{CF4} and E_{C2F6} from the 2019 Refinement of the 2006 IPCC Methodology Report for National GHG Inventory Reporting[7]

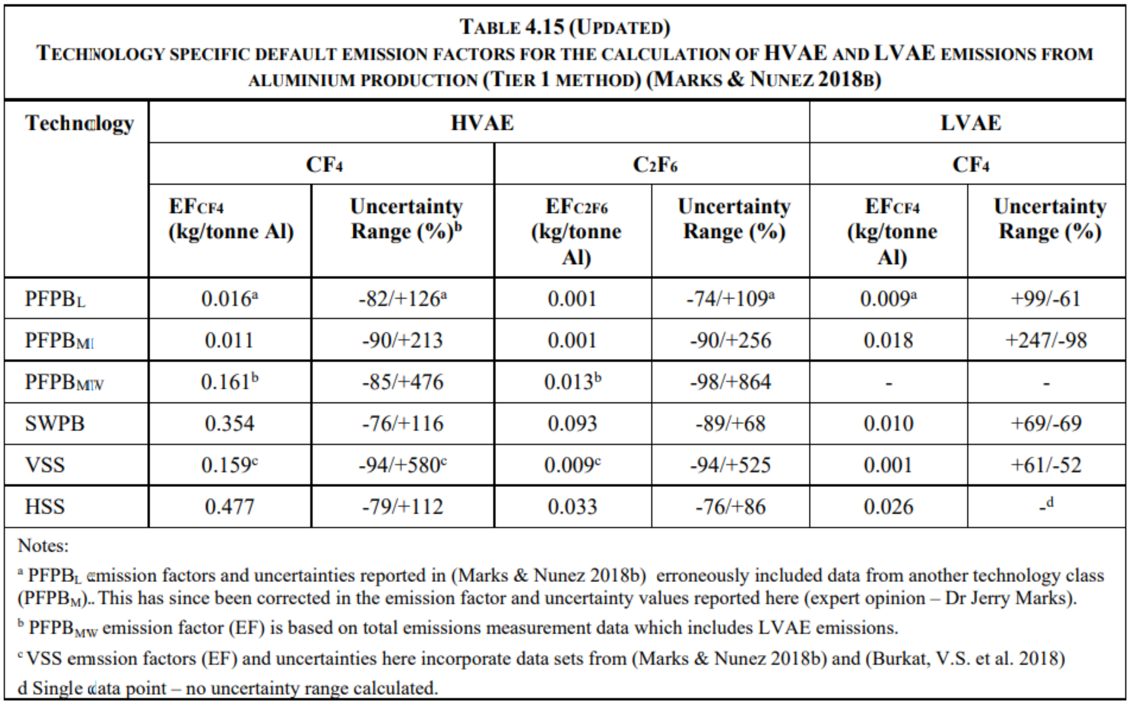

TABLE 4.15 (UPDATED)
TECHNOLOGY SPECIFIC DEFAULT EMISSION FACTORS FOR THE CALCULATION OF HVAE AND LVAE EMISSIONS FROM ALUMINIUM PRODUCTION (TIER 1 METHOD) (MARKS & NUNEZ 2018B)

Technology	**HVAE**				**LVAE**	
	CF_4		**C_2F_6**		**CF_4**	
	EF_{CF4} (kg/tonne Al)	**Uncertainty Range (%)[b]**	**EF_{C2F6} (kg/tonne Al)**	**Uncertainty Range (%)**	**EF_{CF4} (kg/tonne Al)**	**Uncertainty Range (%)**
PFPB_{L}	0.016[a]	-82/+126[a]	0.001	-74/+109[a]	0.009[a]	+99/-61
PFPB_{M}	0.011	-90/+213	0.001	-90/+256	0.018	+247/-98
PFPB_{MW}	0.161[b]	-85/+476	0.013[b]	-98/+864	-	-
SWPB	0.354	-76/+116	0.093	-89/+68	0.010	+69/-69
VSS	0.159[c]	-94/+580[c]	0.009[c]	-94/+525	0.001	+61/-52
HSS	0.477	-79/+112	0.033	-76/+86	0.026	-[d]

Notes:

[a] PFPB_{L} emission factors and uncertainties reported in (Marks & Nunez 2018b) erroneously included data from another technology class (PFPB_{M}).. This has since been corrected in the emission factor and uncertainty values reported here (expert opinion – Dr Jerry Marks).

[b] PFPB_{MW} emission factor (EF) is based on total emissions measurement data which includes LVAE emissions.

[c] VSS emission factors (EF) and uncertainties here incorporate data sets from (Marks & Nunez 2018b) and (Burkat, V.S. et al. 2018)

d Single data point – no uncertainty range calculated.

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[7] (i) Legacy Point-Fed Prebake (PFPBL) – older cell designs with line currents of less than 350kA;
(ii) Modern Point-Fed Prebake (PFPBM) – new cell technologies 5 that operate at line currents in excess of 350kA including: AP3X/AP4X, APXe/AP60, EGA DX and DX+;
(iii) Modern Point-Fed Prebake without fully automated anode effect intervention strategies for PFC emissions (PFPBMW) – new cell technologies operating with large cells with line currents often in excess of 350kA, with no automatic anode effect intervention capacity
(iv) Side-Worked Prebake (SWPB) technology;
(v) Horizontal Stud Søderberg (HSS) technology; and
(vi) Vertical Stud Søderberg (VSS) technology

TABLE 4.16 (UPDATED)
TECHNOLOGY SPECIFIC COEFFICIENTS FOR THE CALCULATION OF HVAE PFC EMISSIONS FROM ALUMINIUM PRODUCTION USING SLOPE[10] METHODOLOGY (TIER 2A METHOD) (MARKS & NUNEZ 2018B)

Technology	**CF_4**		**Weight Fraction C_2F_6/CF_4**	
	SC_{CF4} (kg CF_4/tonne Al)/(AE-Mins/cell-day) [a]	**Uncertainty Range (%)**	**C_2F_6/CF_4**	**Uncertainty range (%)**
$PFPB_L$	0.122	-48/+45	0.097	-35/+31
$PFPB_M$	0.104	-27/+32	0.057	-55/+55
$PFPB_{MW}$[a]	-	-	-	-
SWPB	0.233	-27/+44	0.280	-55+58
VSS	0.058	-53/+130	0.086	-76/+236
HSS	0.165	-47/+28	0.077	-61/+48

Note:

[a] Tier 2 default coefficients are not available for $PFPB_{MW}$ technology class (Modern PFPB without fully automated anode effect intervention strategies for PFC emissions) because process data for anode effect frequency and duration was either not available, or, not comparable to traditional definitions or thresholds associated with anode effects.

TABLE 4.16A (NEW)
SPECIFIC HVAE-CF_4 EMISSION RATE COEFFICIENTS BASED ON THE ANODE EFFECT DURATION AS CALCULATED BY (MARKS & NUNEZ 2018A) (TIER 2B METHOD).

AED[a]	**Value of K_1**	**Value of K_2**
1s < AED ≤5s	0.0341	0.756
5s > AED≤200s	0.0473	0.693
AED >200 s	0.1661	0.479

[a] In the rare occurrences where AED is equivalent to 0s, the equation that should be used is: kg $CF_4 = 0.576 \cdot kA/1000$

EQUATION 4.27F (NEW)
EMISSION RATE COEFFICIENTS FOR HVAE PFC (TIER 2B METHOD – (DION *ET AL.* 2018A))

$$C_1 = 0.6415 \bullet MP_{Day} + 5.878$$

$$C_2 = -0.0972 \bullet MP_{Day} + 0.8905$$

$$C_3 = 0.238 MP_{Day}^2 - 1.407 \bullet MP_{Day} + 2.342$$

$$C_4 = -0.0981 MP_{Day}^2 + 0.381 \bullet MP_{Day} + 0.3413$$

Where :

C_1 = Emission rate coefficient for CF_4 dependant on the metal production of the cell, g CF_4 / s · tonne Al

C_2 = Emission rate coefficient for CF_4 dependant on the metal production of the cell, dimensionless

C_3 = Emission rate coefficient for C_2F_6 dependant on metal production of the cell, g C_2F_6 / s · tonne Al

C_4 = Emission rate coefficient for C_2F_6 dependant on the metal production of the cell, dimensionless.

MP_{Day} = Average daily metal production per cell[11], for the cell technology, tonnes Al

TABLE 4.16B (NEW)
UNCERTAINTY RANGE[C] (%) IN ESTIMATING PFC EMISSIONS FROM INDIVIDUAL HVAES (TIER 2B METHODS)

Technology	**CF_4 [a,b]**		**C_2F_6 [a,b]**	
	Marks & Nunez approach	**Dion *et al.* approach**	**Marks & Nunez approach**	**Dion *et al.* approach**
SWPB	-	-36 / +51	-	-42 / +68
$PFPB_L$	-47 / +29	-36 / +51	-52 / +39	-42 / +68
$PFPB_M$	-16 / +134	-33 / +61	-54 / +152	-24 / +13

Note:

[a] Uncertainty ranges were evaluated for total emissions across multiple measurement campaigns and facilities (expert opinion). Overall, 11 measurement campaigns for $PFPB_M$ and 10 measurements campaigns with $PFPB_L$ or SWPB technology classes were used to estimate the uncertainties related to CF_4, while 5 measurement campaigns for $PFPB_M$ and 4 measurements campaigns with $PFPB_L$ or SWPB technology classes were used to estimate the uncertainties related to C_2F_6 .

[b] Uncertainty ranges were calculated for HVAE emissions, where HVAEs were within the recommended HVAE duration (AED) limits of the (Dion *et al.* 2018a) method. It is possible that the uncertainty increases if the AED exceeds recommended limits when using the (Dion *et al.* 2018a) method, i.e. 1000 s and 150 s for CF_4 and C_2F_6 estimations, respectively.

[c] The uncertainty range calculated in Table 4.16B is based on a comparison with direct measurements and should not be compared to the reported Tier 2a uncertainty range from table 4.16 which compares variations of EF. For comparison, the calculated CF_4 uncertainty range for Tier 2a based on direct measurements is (-44% / + 388%) for legacy facilities and (-22% / + 256%) for modern facilities. The calculated C_2F_6 uncertainty range for Tier 2a based on direct measurements is (-58% / + 8%) for legacy facilities and (-19% / +97 %) for modern facilities.

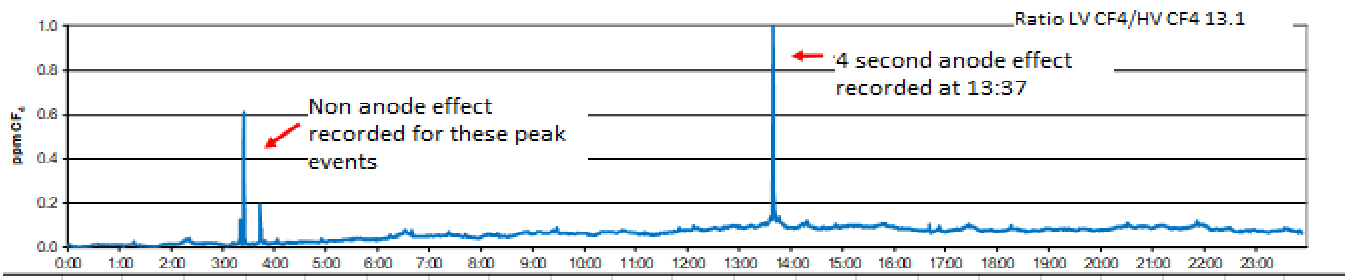
Appendix 2 - Differentiating HV and LV PFC Emissions

The following 24 hour run charts contrast LV and HV CF_4 emissions from two different facility measurements:

a) Figure 4 -from a potline operating with a modern PFPB cell technology sampling the combined exhaust of 44 cells with AEF <0.1, and,

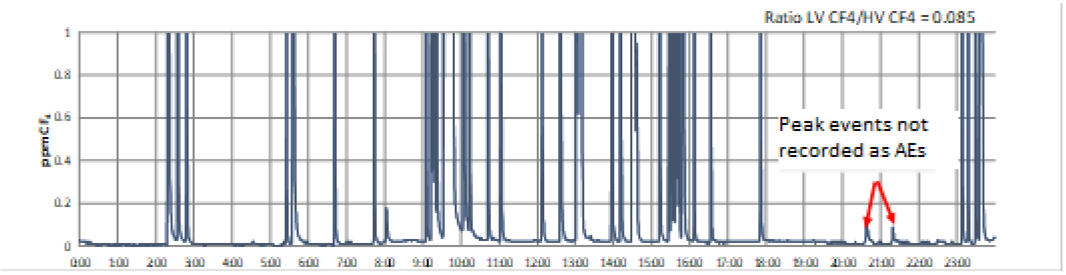
b) Figure 5 - from a measurement made on a potline operating with legacy PFPB cell technology sampling the combined exhaust of 56 cells operating with an AEF of 0.4.

Figure 4 – 24-Hour Run Chart for Modern PFPB Technology Measurement



The chart for the modern PFPB shows the concentration of LV CF_4 at the start of the day at 0.01 ppmv CF_4 and rising to a level of almost 0.1 ppmv just before the recorded HV event at 13:30. The peaks that occurred between 3:00 and 4:00 were not recorded by the process control system as anode effects and are included as LV emissions. CF_4 emissions for this potline, like most high performing PFPB potlines, is dominated by LV emissions with a LV/HV weight ratio greater than 13. Total HV emissions were measured to be 0.0008 kg CF_4/t Al for this potline.

Figure 5 – 24-Hour Run Chart for Legacy PFPB Measurement



The CF_4 concentration recording for the Legacy PFPB potline, in contrast to that of the Modern PFPB line, is dominated by peaks from HVAE events recorded by the process control system. The LV CF_4 emissions are quite low throughout the 24-hour period with concentrations ranging from 0.01 to 0.02 ppmv in the combined gas stream with the exception of two small peak events at 20:30 and 21:30 that were not recorded as HVAE events by the process control system. Total HV emissions for this potline was measured to be 0.08 kg CF_4/t Al and the LV/HV weight ratio measured was 0.085. When measuring LV emissions at the low levels shown in the Legacy run chart it is important to consider and document the uncertainty levels for these measurements.

In practice, to measure HV and LV emission factors, HV emissions are first calculated by correcting peak area emissions for background. It's convenient to plot start times of recorded HV events on the same run chart as the CF_4 concentration to be sure that no LV events are included in the total. The second step is to calculate total emissions, HV plus LV. Finally, LV emissions are calculated by difference, total minus HV. For these at line FTIR measurements where CF4 concentration for LVAE ranges from 0.01 to 0.02 ppmv the uncertainty is estimated to be +/-100% of the measured amount. However, for measurements such as that shown for the Modern PFPB technology the uncertainty is estimated to range from +/-20% to +/-10% depending on the concentration of the LV emissions.

Appendix 3 - Guidance and Checklist for third party providers

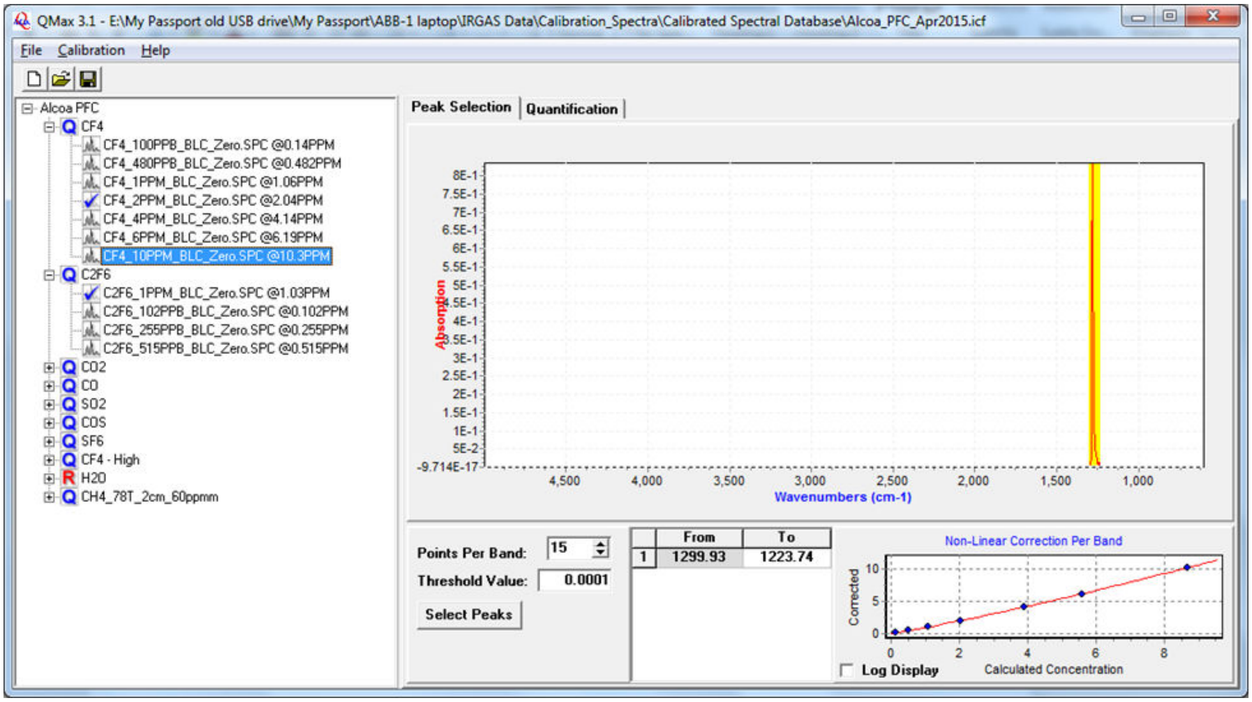
Detailed analytical procedures for checking third party companies use reliable infrared instruments to measure gas emissions are summarized below. Extractive Fourier Transform Infrared (FTIR) Spectrometry measures multiple components in the off-gases emissions from the aluminum production process. Gases that are measured are carbon dioxide, CO2, carbon monoxide, CO, carbonyl sulfide, COS, sulfur dioxide, SO2, hydrogen fluoride, HF, and both Perfluorocarbon (PFC) tetrafluoro methane, CF_4 and hexafluoro ethane, C_2F_6.
Calibration:

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:

$$Ai = ai\ b\ ci$$

Ai = absorbance at a given frequency of the ith sample component
ai = absorption coefficient (absorptivity) of the ith sample component
b = path length of the cell
ci = concentration of the ith sample component

The instrument should be calibrated in the range for expected CF_4 and C_2F_6 emissions. Third party company requirement is to measure CF_4 in the 0.010-10 ppm and C_2F_6 in the 0.020-1 ppm ranges. Simultaneous pot starts might require extending the range to 100 ppm CF_4 and 10 ppm C_2F_6. Figure 6 shows a calibration example.



Points Per Band: 15
Threshold Value: 0.0001

	From	To
1	1299.93	1223.74

☐ Log Display

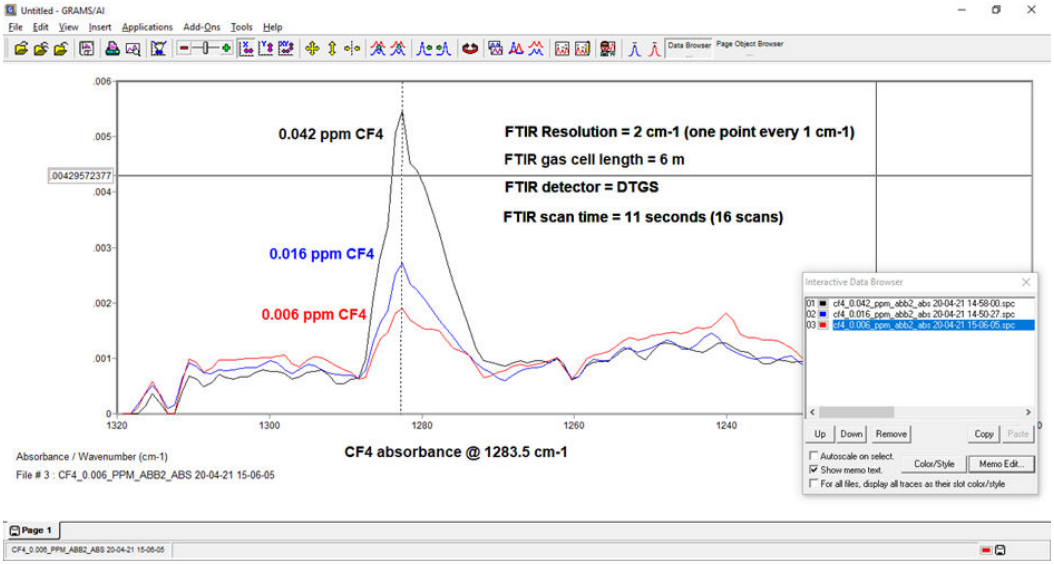
Figure 6: CF4 calibration example

The preferred frequency measurement time for each scan is 11, 15 or 20 seconds and is set up in the FTIR parameters settings. This time is necessary to capture very short duration anode effects.

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 certificate of analysis for the gases used in the CF_4 and C_2F_6 calibrations.

1. <u>Limit of detection:</u>

There are different FTIR manufacturers that can offer configuration options for the optical path in gas cell, detector and resolution among others. The third-party company should state how low CF4 can be detected and provide infrared spectra that shows confirmation of the CF_4 absorbance band detection at 1283 cm-1.
Figure 2 shows analytical response of diluted samples of CF_4 standards using a 6m gas cell, DTGS detector, 2 cm-1 resolution, and 11 sec scan time of FTIR CIC Photonics brand.


FTIR Resolution = 2 cm-1 (one point every 1 cm-1)
FTIR gas cell length = 6 m
FTIR detector = DTGS
FTIR scan time = 11 seconds (16 scans)

01 cf4_0.042_ppm_abb2_abs 20-04-21 14-58-00.spc
02 cf4_0.016_ppm_abb2_abs 20-04-21 14-50-27.spc
03 cf4_0.006_ppm_abb2_abs 20-04-21 15-06-05.spc

☐ Autoscale on select.
☑ Show memo text.
☐ For all files, display all traces as their slot color/style

Absorbance / Wavenumber (cm-1)
File # 3 : CF4_0.006_PPM_ABB2_ABS 20-04-21 15-06-05

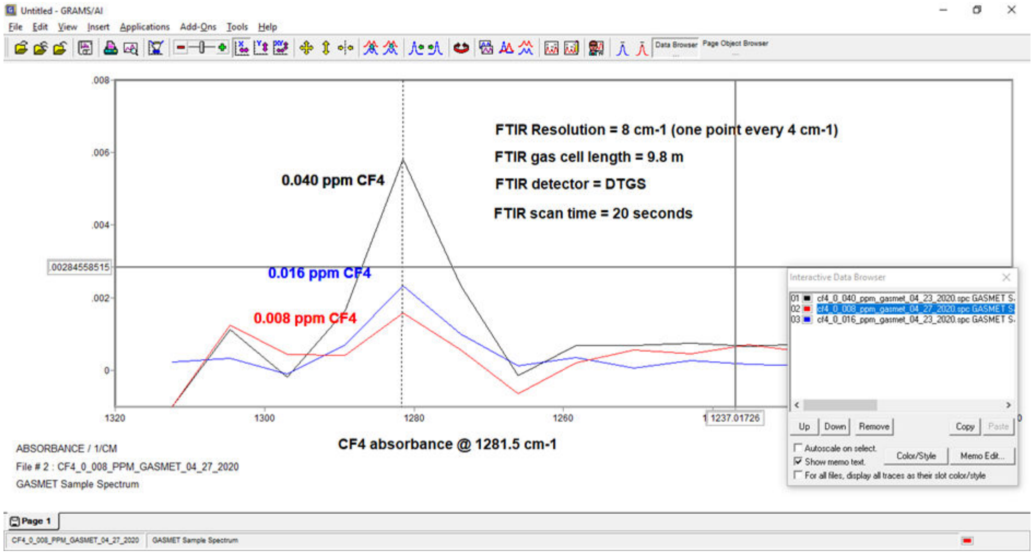
Figure 7: CF4 measured spectra using CIC Photonics FTIR

The CF_4 spectra shows decreased absorbance intensities from 0.042 ppm (42 ppb) to 0.006 ppm (6 ppb) at 1283.5 cm-1 and confirm low voltage PFC emissions and short duration high voltage PFC emissions can be measured continuously, if they are above 6ppb, with a scan frequency of 11 seconds.

Figure 8 shows analytical response of diluted samples of CF_4 standards using a 9.8 m gas cell, DTGS detector, 8 cm-1 resolution, and 20 sec scan time of FTIR Gasmet brand.

The CF_4 spectra shows decreased absorbance intensities from 0.040 ppm (40 ppb) to 0.008 ppm (8 ppb) at 1281.5 cm-1 and confirm low voltage PFC emissions and short high voltage PFC emissions can be measured continuously, if they are above 8 ppb, with a scan frequency of 20 seconds. However, Gasmet FTIR uses a lower resolution that is 8 cm-1, which does not resolve (or add more points) to the CF_4 peak as it does the CIC Photonics FTIR brand, which spectra was obtained at 2 cm-1 resolution.

Gasmet FTIR is a popular instrument due to its portability but only measures spectra using 8 cm-1 resolution, which might be a limitation to prove very short high voltage anode effects or low voltage emissions <8 ppb are occurring.



FTIR Resolution = 8 cm-1 (one point every 4 cm-1)
FTIR gas cell length = 9.8 m
FTIR detector = DTGS
FTIR scan time = 20 seconds

01 cf4_0_040_ppm_gasmet_04_23_2020.spc GASMET S.
02 cf4_0_008_ppm_gasmet_04_27_2020.spc GASMET S.
03 cf4_0_016_ppm_gasmet_04_23_2020.spc GASMET S.

☐ Autoscale on select.
☑ Show memo text.
☐ For all files, display all traces as their slot color/style

File # 2 : CF4_0_008_PPM_GASMET_04_27_2020
GASMET Sample Spectrum

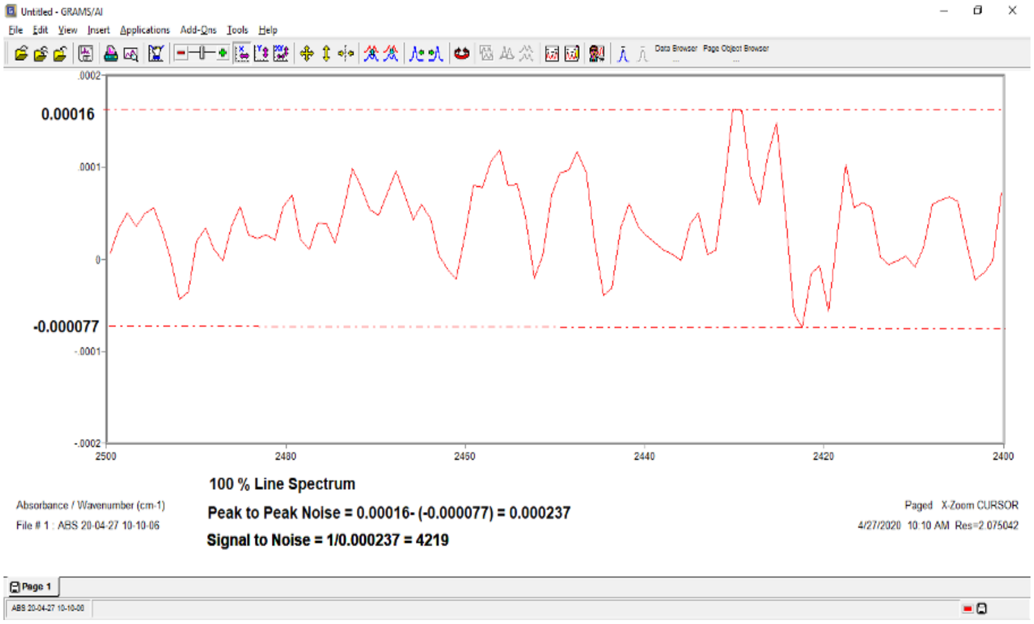
CF4_0_008_PPM_GASMET_04_27_2020 | GASMET Sample Spectrum

Figure 8: CF4 measured spectra using Gasmet FTIR

2. Signal to Noise Ratio:

Infrared absorption spectroscopy is performed by directing an infrared beam through a sample to a detector. The frequency-dependent infrared absorbance of the sample is measured by comparing this detector signal (sample single beam spectrum) to a signal obtained without a sample in the beam path (background single beam spectrum). 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. Figure 9 shows CIC Photonics FTIR zero-absorbance Signal to Noise in the 2500-2400 cm-1 range.



100 % Line Spectrum

Absorbance / Wavenumber (cm-1)

File # 1 : ABS 20-04-27 10-10-06

Peak to Peak Noise = 0.00016- (-0.000077) = 0.000237

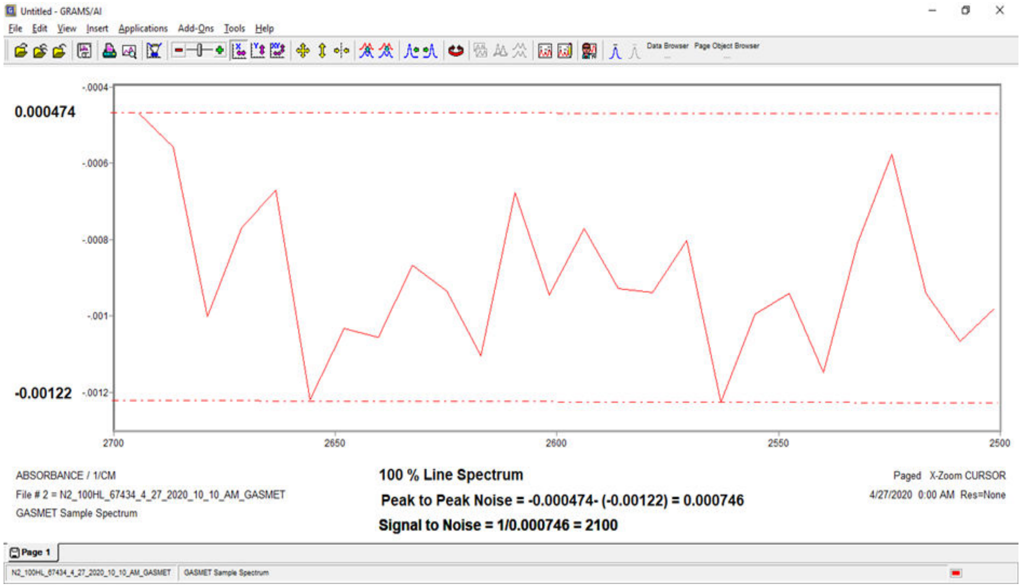
Signal to Noise = 1/0.000237 = 4219

Paged X-Zoom CURSOR

4/27/2020 10:10 AM Res=2.075042

Figure 9: CIC Photonics FTIR showing zero-absorbance Noise for 11 seconds measurement time

The peak-to-peak Signal to Noise value for CIC Photonics FTIR is calculated by the inverse of the subtraction difference and is equal to 4219. Figure 10 shows Gasmet FTIR zero-absorbance Signal to Noise in the 2700-2500 cm-1 range. The peak-to-peak Signal to Noise value calculated for Gasmet FTIR is 1340.



ABSORBANCE / 1/CM

File # 2 = N2_100HL_67434_4_27_2020_10_10_AM_GASMET

GASMET Sample Spectrum

100 % Line Spectrum

Peak to Peak Noise = -0.000474- (-0.00122) = 0.000746

Signal to Noise = 1/0.000746 = 2100

Paged X-Zoom CURSOR

4/27/2020 0:00 AM Res=None

Figure 10: Gasmet FTIR showing zero-absorbance Noise for 20 seconds measurement time

The checklist below identifies some common factors that can impact reliable results when measuring PFC emissions. These are provided as an example of ‘things to check’ when liaising with third party companies.

- Instrument not adequate (for example inappropriate pathlength in gas cell, high LOD, etc);
- No sampling filters used or delay in replacing filter to avoid water interference (e.g. Drierite);
- Lack of expertise in FTIR for trace quantification (optimize resolution, scan time, detector);
- Bad calibration (not linear, out of range, lack of standard certification, few standards);
- Lack of daily Nitrogen zero background collection that can lead to FTIR drift;
- Urgency of finishing sampling without proper collection of number of anode effects;
- Inaccuracies in low voltage measurement;
- Occurrence of operational event that is atypical of ongoing operations such as a long power outage;
- Delay in reporting results after on-site measurements are finished (ideally sampling and calculation should be supervised).

It is recommended to request third party companies provide comprehensive information on the plan for a measurement campaign before a request is sent to conduct PFC measurements. This should include the points above along with critical information such as the specific FTIR equipment, parameters to be used, previous experience/expertise. It may be worthwhile to conduct comparative tests with their equipment or to provisionally supervise the measurements undertaken on-site in order to standardize the process as much as possible. Round-robin testing with other techniques can also assist in identifying possible issues before and during measurements.

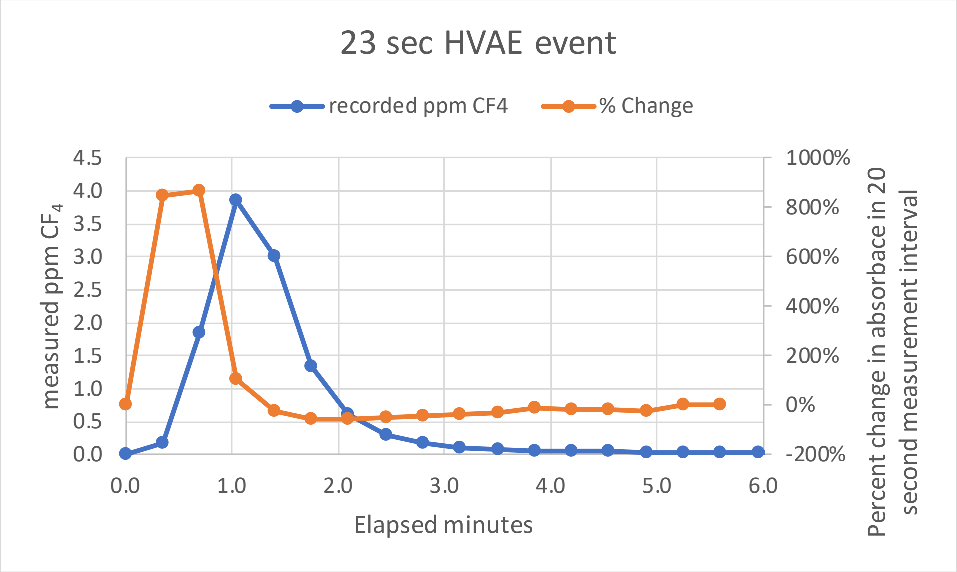
Appendix 4 – Suppliers of Equipment for PFC Measurement

1. Infrared Measurement Instruments include MKS, ABB CIC Photonics, Midac and Gasmet DX4000 spectrometerand prototype laser spectrometers.
2. Gas sample collection bags that have proven effective for collecting and holding PFC samples for a period more than three months without loss are provided by Calibrated Instruments, Inc. - www.calibrated.com.
3. Stainless steel canisters are available from Restek - www.restek.com and Entech - www.entechinst.com.
4. Activated alumina formed into 1/8 inch balls is available from Adcoa - www.adcoa.net.
5. DryCal Defender Series Flow Calibrator available from Mesa Labs - www.drycal.mesalabs.com, a battery-operated flow measurement device for injecting tracer gas into the smelter exhaust system for quality control check on duct flow rate and on measurement system performance.
6. Balston filters sometimes used in the upstream is available here: www.balstonfilters.com.

Appendix 5 – Method 2: Direct Measurement by real time extractive sampling for a limited time

A. Sampling approach and Instrument

The rapid rate of change in measured concentration of CF_4 in the sample stream is illustrated in the graphic shown here of the apparent ppm CF_4 measured for a 23 second recorded HV event.



The velocity of the gas stream in the smelter fume collection system is very fast. Emissions from any individual cell arrive at the chimney exhaust within seconds from the time the event begins. In many instances the transit time from the sample probe through the sample tubing to the instrument is longer than the transit time from the reduction cell to the chimney. The illustration graphic was produced from measurement with a Gasmet DX4000 FTIR instrument which measures the entire IR region 20 times each second. Because there is such a great volume of data produced the interferograms are averaged over periods from 1 second to three minutes to reduce the data reduction effort. The example shown shows results for 20 second averages of interferograms, thus includes the results for 400 individual scans. The illustrated HVAE profile shows a maximum recorded concentration of about 4 ppm CF_4, however, the rate of change in measured 20 second averages would indicate that the instantaneous concentration at any given moment during the 20 seconds might have been considerably higher than the average recorded 4 ppm.

There are two implications of this rapidly changing signal. First, care must be taken to choose a sampling point where transient concentrations does not exceed the range of linearity of the measurement device. Secondly, for devices that only sample the gas stream periodically a sampling accommodation, such as an accumulator, should be made to assure that the emissions are accurately tracked.

B. Calculating Emission Factors Based on direct Measurement by real time extractive sampling for a limited time

This section presents the calculations for specific emissions of CF_4 and C_2F_6, as well as for the facility-specific slope and overvoltage parameters, when direct at line measurements of PFCs are made.

Step 1: For each time increment for which the instrument reports PFC concentrations calculate the kg CF_4 and C_2F_6.

Total kg CF_4 *for the instrument measurement increment =*

C (μ *l* CF_4*/l air)* $\times$ *(1 l* CF_4*/*$10^6 \mu$ *l* CF_4*)* $\times$ *(1mole* CF_4*/22.4l* CF_4*)* $\times$ *0.0880 (kg* CF_4*/mole* CF_4 *)* $\times$ *1000 (l air/*m^3 *air (0ºC, 1atm))* $\times$ *F (*m^3 *air @ 0ºC, 1atm)*

Total kg C_2F_6 *for the instrument measurement increment =*

C (μ *l* C_2F_6*/l air)* $\times$ *(1 l* C_2F_6*/*$10^6 \mu$ *l* C_2F_6*)* $\times$ *(1 mole* C_2F_6*/22.4l* C_2F_6*)* $\times$ *0.138 (kg* C_2F_6*/mole* C_2F_6*)* $\times$ *1000 (l air/*m^3 *air (0ºC, 1atm))* $\times$ *F (*m^3 *air @ 0ºC, 1atm)*

Where:
F = Air flow for each time increment (m^3 at 0°C and 1 atm)
C = CF_4 or C_2F_6 concentration, ppmv

Step 2: Sum the total kg CF_4 and C_2F_6 for the total sampling period.

Total kg CF_4 *= sum from time =* t_1 *to time =* t_2 *of all the kg* CF_4 *for each instrument reporting period*

$$Total \quad kg\ CF_4 \quad = \quad \sum_{t_1}^{t_2} kg\ CF_4$$

Where:
t_1 = Start of continuous sampling period
t_2 = End of continuous sampling period

Total kg C_2F_6 *= sum from time =* t_1 *to time =* t_2 *of all the kg* C_2F_6 *for each instrument reporting period*

$$Total \quad kg\ C_2F_6 = \quad \sum_{t_1}^{t_2} kg\ C_2F_6$$

Where,
t_1 = Start of continuous sampling period
t_2 = End of continuous sampling period

Step 3: Calculate the aluminum production for the sampling period as in Appendix 6, Step 5.

Step 4: Calculate the emission rates, CF_4 per metric ton Al slope coefficient and weight ratio of C_2F_6/CF_4 as in Appendix 6, Steps 4 through 9.

Appendix 6 – Method 3: Direct Measurements of an average sample and post sampling analysis

Calculating Emission Factors Based on Direct Measurements of an average sample and post sampling analysis

This section presents equations for calculating emissions for CF_4 and C_2F_6 per metric ton aluminum when measurements are made on time average samples using sample bags or canisters. Equations are also presented for calculating slope and overvoltage coefficients from the PFC emissions per metric ton aluminum and the weight ratio of C_2F_6 to CF_4. The slope and overvoltage factors are the coefficients in the IPCC Tier 3 method for inventory of PFCs based on anode effect data. Each of the recommended 10 steps is described below. Note that Tier 3 slope and overvoltage factors cannot be determined by this method independently when LV CF4 emissions are present as this method does not differentiate.

Step 1: Calculate total gas flows for the sampling period for each duct sampling location and for pot room rooftop flows when fugitive measurements are made.

- Step 1a: Calculate the fume collection duct flow rate after measuring average gas velocity, duct cross-sectional area, duct temperature, and duct pressure:

  $$f = V \times S \times 273/(T+273) \times P/760 \times 3600$$

  Where:

  f = Flow rate (m^3/h at 0ºC and 1atm)

  V = Average gas velocity (m/s)

  S = Duct cross-sectional area (m^2)

  T = Duct temperature (ºC)

  P = Duct pressure (mm Hg)

  273 = Addition factor converting *ºC to ºK*

  3600 = Factor converting hours to seconds (3600 s/hr)

  760 = Atmospheric pressure (mm Hg)

  Calculate total flow, F, for the sampling period in m^3 at 0°C and 1 atm:

  $$F = f \times t$$

  Where:

  F = Total flow (m^3 at 0°C and 1 atm)

  f = Flow rate (m^3/h at 0ºC and 1atm)

t = Sampling time (h)

- Step 1b. Similarly, calculate the total flow through the potroom rooftop:

$$f = V \times S \times 273/(T+273) \times P/760 \times 3600$$

Where:
f = Rooftop flow rate (m^3/h at 0ºC and 1atm)
V = Roof monitor average gas velocity (m/s)
S = Roof monitor cross-sectional area (m^2)
T = Average rooftop temperature (ºC)
P = Rooftop pressure (mm Hg)
273 = Addition factor converting *ºC to ºK*
3600 = Factor converting hours to seconds (3600 s/hr)
760 = Atmospheric pressure (mm Hg)

Step 2: Calculate total kg CF_4 for sampling period captured by the exhaust duct and the kg CF_4 per anode effect minute for the sampling period.

- Step 2a. Calculate the total kg CF_4 for sampling period captured by the exhaust duct.

$$\text{Total kg } CF_4 \text{ captured by duct for the sampling period (kg } CF_{4\ \text{duct}}\text{) =}$$
$$C\ (\mu\text{ l } CF_4/\text{l air}) \times (1\text{ l } CF_4/10^6 \mu\text{ l } CF_4) \times (1\text{ mole } CF_4/22.4\text{l } CF_4) \times 0.0880\ (\text{kg } CF_4/\text{mole } CF_4) \times 1000\ (\text{l air}/m^3\text{ air (0ºC, 1atm)}) \times F\ (m^3\text{ air @ 0ºC, 1atm})$$

Where:
C = Time average CF_4 concentration (μl CF_4/l air) = ppmv CF_4

- Step 2b. Calculate the total kg CF_4 per anode effect minute captured by the duct for the sampling period by dividing the total kg CF_4 from step 2a by the total anode effect minutes recorded for the test section during the sampling period.

$$\text{Average kg } CF_{4\ \text{duct}}/\text{AE minute = total kg } CF_{4\ \text{duct}}/\Sigma\ \text{(duration of all anode effects in sample period) (min)}$$

Step 3: Calculate total kg C_2F_6 for the sampling period captured by duct.

$$\text{Total kg } C_2F_6 \text{ captured by duct for the sampling period (kg } C_2F_{6\ \text{duct}}\text{) =}$$
$$C\ (\mu\text{ l } C_2F_6/\text{l air}) \times (1\text{l } C_2F_6/10^6 \mu\text{ l } C_2F_6) \times (1\text{ mole } C_2F_6/22.4\text{ l } C_2F_6) \times 0.138\ (\text{kg } C_2F_6/\text{mole } C_2F_6) \times 1000\ (\text{l air}/m^3\text{ air (0ºC, 1atm)}) \times F\ (m^3\text{ air @ 0ºC, 1atm})$$

Step 4: Calculate the weight ratio of C_2F_6 to CF_4:

$$Ratio_{C_2F_6/CF_4} = kg\ C_2F_{6\ duct} / kg\ CF_{4\ duct}$$

Step 5: Calculate p, the total aluminum production for the duct sampling period:

$$p\ (metric\ ton\ Al) = P\ (metric\ ton\ Al/cell\text{-}day) \times N\ (cells) \times t(h)/24(h/day)$$

Where:

P = Aluminum production rate (metric ton Al/cell-day)

N = Number of operating cells in sampled section

t = Sampling duration (hrs)

Step 6: Calculate PFCs emitted as fugitive emissions.

- Step 6a. When fugitive PFC emissions are estimated based on exhaust system collection efficiency, calculate fugitive CF_4 and C_2F_6 as a fraction of total PFC emissions as follows:

  $$kg_{CF_4\text{-fugitive}} = kg_{CF4\text{-duct}} \times Fraction_{fugitive} /(1- Fraction_{fugitive})$$

  $$kg_{C_2F_6\text{-fugitive}} = kg_{C_2F_6\text{-duct}} \times Fraction_{fugitive} /(1- Fraction_{fugitive})$$

- Step 6b. When fugitive PFC emissions are measured, measurement can be made by direct open path FTIR spectrometry, by the time average bag method or other methods shown to be capable of measuring the PFC emissions not captured by the duct system. The equations below are based on the time average bag method or column sorbent method. However, they also apply to FTIR measurements by use of the average CF_4 concentration measured by the FTIR process rather than the average concentration calculated in Step 6b.1:

  - Step 6b.1. First calculate the average CF_4 concentration from the rooftop bag or sorbent column samples for each sampling period:

    $$C_{CF_4\text{-avg}} = (C_{bag1} + C_{bag2} + C_{bag3} \ldots + C_{bag\ n.})/(Total\ number\ of\ bag\ samples\ n)$$

  - Step 6b.2. Next, similar to the method in Step 2 above, convert the average bag CF_4 concentration into kg CF_4 emitted from the potroom rooftop for the sampling period by multiplying by the total potroom ventilation flow through the rooftop from Step 1b for the sampling period.

Total kg CF_4 emitted as fugitive emissions for the sampling period =

$kg_{CF_4\text{-fugitive}} = C_{CF4\text{-avg}}\ (\mu l\ CF_4/l\ air) \times (1l\ CF_4/10^6 \mu\ l\ CF_4) \times (1mole\ CF_4/22.4\ l\ CF_4) \times 0.0880\ (kg\ CF_4/mole\ CF_4) \times 1000\ (l\ air/m^3\ air\ (0ºC,\ 1atm)) \times F\ (m^3\ air\ @\ 0ºC,\ 1atm)$

Where:

F = total flow through potroom rooftop for sampling period (m^3 air at 0ºC and 1atm)

- Step 6b.3. Next, calculate the fugitive kg CF_4 per anode effect minute by dividing the total kg CF_4 emitted as fugitive emissions from Step 6b.2 by the total anode effect minutes for the entire potroom for the sampling period.

($kg\ CF_4$/AE minute)$_{fugitive}$ = Total kg CF_4 emitted as fugitive emissions for the sampling period calculated from Step 6a or Step 6b.2 divided by the total anode effect minutes for the potroom for the fugitive sampling period.

- Step 6b.4. Calculate the fraction of total PFC emissions emitted as fugitives, $Fraction_{fugitive}$, by dividing the (kg CF_4/AE minute)$_{fugitive}$ from Step 6b.3 by the sum of (kg CF_4/AE minute)$_{duct}$ from Step 2b and the (kg CF_4/AE minute)$_{fugitive}$ as follows.

$Fraction_{fugitive} = (kg\ CF_4/AE\ minute)_{fugitive}/[(kg\ CF_4/AE\ minute)_{fugitive} + (kg\ CF_4/AE\ minute)_{duct}]$

Step 7: Calculate the emission rates in kg CF_4/metric ton Al and kg C_2F_6/metric ton Al for the combined duct measurement and fugitive emissions. The total kg CF_4 emissions are equal to the sum of the fugitive CF_4 emissions and the CF_4 emissions measured in the duct. The total kg CF_4 emissions are then calculated from the fugitive fraction, $Fraction_{fugitive}$, as follows. The $Fraction_{fugitive}$ is the value from Step 6b.4 if fugitives are measured. Otherwise, if fugitives are calculated from the collection fraction, the fugitive fraction is estimated based on collection fraction data from fluoride collection efficiency or other documented criteria.

- Step 7a. Calculate total CF_4 emissions adjusted to include fugitive emissions

$Total\ kg\ CF_4 = kg\ CF_{4duct}/(1-Fraction_{fugitive})$

Where:

kg $CF_{4\ duct}$ = kg CF_4 obtained in Step 2a.

$Fraction_{fugitive}$ = Fugitive fraction from Step 6b.4., if fugitives are measured, or, calculated fugitive fraction based on collection efficiency.

- Step 7b. Then calculate the rate for CF_4 emissions per metric ton Al.

R_{CF4} = (*Total kg CF_4 for the sampling period)/ p metric ton Al)*

Where:

R_{CF4} = Aluminum specific CF_4 emission rate (kg CF_4/metric ton Al)

Total kg CF_4 for the sampling period = CF_4 emissions, including both duct and fugitive emissions (from Step 7a.)

p = Metric tons primary aluminum production (from Step 5) (metric ton Al)

- Step 7c. Calculate the emission rate for C_2F_6 per metric ton Al as follows.

$$R_{C2F6} = R_{CF4} \times Ratio_{C_2F_6/CF_4}$$

Where:

R_{C2F6} = C_2F_6 emission rate (kg C_2F_6/metric ton Al)

R_{CF4} = CF_4 emission rate from Step 7b. (kg CF_4/metric ton Al)

Ratio $_{C_2F_6/CF_4}$ = Weight ratio of emissions of C_2F_6 to CF_4 from Step 4 (decimal fraction)

Step 8: Calculate CF_4 slope, S_{CF4}.

$$S_{CF4}\ (\text{Total kg } CF_4/\text{metric ton Al})/(\text{AE min/cell-day}) = (R_{CF_4})/(\text{AE min/cell-day})$$

Where:

R_{CF4} = CF_4 emission rate from Step 7b (kg CF_4/metric ton Al)

AE min/cell-day = Total anode effect minutes recorded for the cells in the test section for the period over which kg CF_4 is measured in the duct divided by the calculated cell days in the test section for the same period.

Step 9: If applicable, calculate CF_4 overvoltage coefficient. The overvoltage factor is expressed as kg CF_4-%CE / metric ton Al / millivolts.

$$\text{Overvoltage factor}_{CF4}\ \{(\text{kg } CF_4 - \%CE)/(\text{metric ton Al} - mV)\} = \text{kg } CF_4/\text{metric ton Al} \times CE/AEO = R_{CF4} \times CE/AEO$$

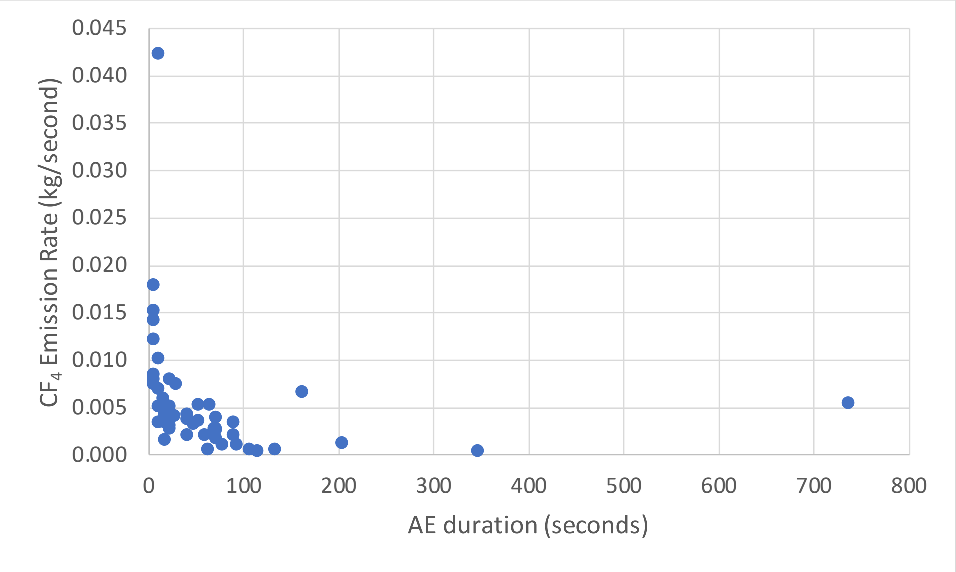
Where:

CE = Current efficiency for aluminum production (percent)

AEO = Overvoltage for the specific cells in the test section during the sampling period (millivolts)

Appendix 7 – CF_4 emissions from individual anode effects

Typical data for the relationship of CF_4 emissions from individual anode effects versus the duration of the anode effects is illustrated in the graphic below.



The average rate for CF_4 emissions drops significantly at longer durations. The slope model calculates the CF4 emission factor as the average ratio of kg CF_4 per anode effect minute to the metal production rate, tonnes Al per cell day. In order for the Tier 3 CF4 coefficient to accurately calculate emission inventories after the measurement the distribution of anode effect durations must remain similar to the distribution during the measurement. In particular several long anode effects during a 72-hour measurement, as recommended in the 2008 Protocol, can skew the calculated slope to lower values and may not be representative of the long-term duration distribution.

Calculation of CF_4 emissions using the IPCC Tier 2 slope coefficient results in high uncertainty in calculated emission factors because the Tier 2 coefficient is the average of measured Tier 3 slope coefficients for a reduction technology group. There can be considerable differences for different operators in anode effect process control procedures there resulting in big differences in individual facility anode effect duration distribution from the average distribution from the measurement data base.

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