

Protocol for Measurement of Tetrafluoromethane (CF₄) and Hexafluoroethane (C₂F₆) Emissions from Primary Aluminum Production



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The EPA's Voluntary Aluminum Industry Partnership was launched in 1995 to reduce emissions of PFCs emitted as a byproduct of the aluminum smelting process. VAIP members are Rio Tinto Alcan, Sebree Works; Alcoa, Inc.; Century Aluminum Company; Columbia Falls Aluminum Company; Noranda Aluminum Inc.; and the Aluminum Association.

Preface

The first PFC Measurement Protocol was developed in 2003. This current version builds on the 2003 version, but contains a number of significant updates, incorporating both quantitative and methodological improvements. Some of the key updates include:

- The incorporation of anode effect parameters which reflect recent results presented in the International Aluminium Institute's "Report on the Aluminium Industry's Global Perfluorocarbon Gas Emissions Reduction Programme: Results of the 2005 Anode Effect Survey" (IAI, 2007).
- The utilization of data and estimation methodologies that are consistent with the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. These include: revised slope and overvoltage factors, and the streamlining of Tier 3 coefficients into a single parameter for both slope and overvoltage, thus eliminating the Tier 3a and Tier 3b notation that was utilized in IPCC (2001).
- The measurement of fugitive emissions is recommended only if fugitives are estimated to account for more than 10 percent of total PFC emissions, up from 5 percent in the 2003 version of the protocol. The change reflects additional measurement experience that has shown that fugitive emissions can be estimated with sufficient accuracy from data such as historical fluoride collection efficiency. When the collection fraction is greater than 90 percent, rooftop measurements of fugitive PFC emissions are difficult to make and the uncertainties are comparable with a good estimated value.
- Based on recent measurement experience, some smelting process data requirements that have been shown to be superfluous have been eliminated, while other smelter data that has been shown to be useful has been added to the data collection requirements.
- This version of the protocol also provides more specific guidance on sampling locations.
- Spreadsheet templates have been updated to provide additional assistance in planning for measurements and in formatting measurement results to facilitate and maximize quality assurance.

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1.0 Introduction

The purpose of this Protocol is to foster consistency in smelter-specific sampling programs.¹ The specific objective of the described measurement process is to make measurements of tetrafluoromethane (CF₄) and hexafluoroethane (C₂F₆) that allow the calculation of facility specific emission factors for the accurate estimation of CF₄ and C₂F₆ emissions from primary aluminum production. These emission factors characterize the relationship between facility anode effect performance and periodically or continuously measured PFC. In addition to their role in the development and implementation of anode effect reduction strategies, one of the most important uses of these emission factors is for developing greenhouse gas inventories. The Intergovernmental Panel on Climate Change (IPCC) publishes default Tier 2 smelting technology-specific emission factors, however, as described in IPCC guidance, PFC emission estimates using Tier 3 facility-specific results is significantly higher accuracy.²

1.1 Objective of Measurement Protocol

The specific objective of the measurement process, as described herein, is to make measurements of CF₄ and C₂F₆ and collect pertinent smelter process data that allow the calculation of facility specific emission factors as described in the Intergovernmental Panel on Climate Change (IPCC) Tier 3 method. This document provides the necessary guidance to allow individual facilities to develop detailed plans for sampling and analysis based on plant-specific technology, anode effect data and chosen measurement instrumentation. Use of the protocol will result in more consistency in reports of PFC measurements. Additionally, integration of the new measurement data into future Tier 2 equation coefficients will lead to improved accuracy of IPCC Tier 2 PFC emissions calculations.

Measurements of perfluorocarbons made over a period of several days provide only a short-term view of emissions for the specific section of cells for which the measurement is carried out. Furthermore, day-to-day variations in anode effect frequency and duration, as well as variations in production levels may well change the PFC emissions for the site. The calculation of long-term average emissions based on the Tier 3 methodology accounts for these temporal variations.

1.2 Why Measure PFCs?

Central to any study of climate change is the development of an emissions inventory that identifies and quantifies anthropogenic sources and sinks of greenhouse gases. The most accurate estimates of PFC emissions from primary aluminum make use of facility-specific emission factors based on measurements at the individual production site. In general, industry and governments use inventories to support three major initiatives:

¹ J. Marks, R. Kantamaneni, D. Pape and S. Rand, "Protocol For Measurement of Tetrafluoromethane and Hexafluoroethane From Primary Aluminum Production," *Light Metals* (2003), pp 221 – 226.

² Intergovernmental Panel on Climate Change, 2006 IPCC Guidelines for National Greenhouse Gas Inventories Volume 3, Industrial Processes and Product Use, Chapter 4, Section 4.4, Primary Aluminium Production, http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/3_Volume3/V3_4_Ch4_Metal_Industry.pdf, pp 4.43 – 4.58.

- **Benchmarking and Process Improvement.** Benchmarking is an important management tool that helps companies evaluate emissions, set goals and develop strategies for reducing emissions. The understanding that is developed from measurements of PFC emissions at individual facilities can be the basis for a well-formulated process improvement plan. Accurate inventories of PFC emissions are also important in benchmarking performance against other producers operating with similar technologies.
- **United Nations Framework Convention on Climate Change.** Countries that are signatories of the Framework Convention on Climate Change are responsible for reporting an annual inventory of greenhouse gas emissions. Over one hundred and eighty countries are signatories to the Framework Convention and gather data annually on industrial processes as part of their national inventory. The measurement of PFCs facilitates creation of a more accurate inventory through use of facility specific emission factors rather than default values.
- **Market Mechanisms.** The Kyoto Protocol contains several market mechanisms, including emissions trading, the Clean Development Mechanism (CDM) and Joint Implementation (JI) to provide flexibility and lower overall costs for achieving greenhouse gas emissions reductions. These flexible mechanisms are based on the assignment of a financial value to emission reductions (e.g., US\$ per ton of carbon equivalent reduced). Accurate and verifiable emissions reductions are required to participate in the sale of credits generated under these programs. Facility specific measurements provide the most accurate documentation of PFC emissions reductions. Accepted and validated measurement procedures are important to verify reductions and facilitate trading.

The International Aluminum Institute (IAI) sponsors global surveys of anode effect performance and PFC emissions.³ In the U.S., primary aluminum producers have committed to PFC emissions reductions through the Voluntary Aluminum Industrial Partnership, a voluntary partnership between individual primary aluminum producers and the U.S. EPA. Other countries are also undertaking industry-government initiatives to reduce PFC emissions from aluminum production.⁴ The multilateral Asia Pacific Partnership contains another initiative aimed at reduction of PFC emissions in primary aluminum production.⁵

1.3 Organization of Remainder of This Document

The remainder of this document is organized into nine sections and four appendices.

- 1. Background.** This section describes the PFC sources and release mechanisms during aluminum production.
- 2. IPCC Three-Tiered Approach.** IPCC guidelines for estimating PFC emissions from aluminum production are described.

³ International Aluminium Institute, Perfluorocarbon Compounds Emissions Survey 1990 – 2005, <http://www.world-aluminium.org/iai/publications/documents/pfc2004.pdf>, June, 2006..

⁴ E.J. Dolin, J. Casola and T. Miller, “PFC Emissions in the Aluminum Sector: International Strategies and Reductions,” *Light Metals* (2001).

⁵ <http://www.asiapacificpartnership.org/>

3. **Process Data Requirements.** This section presents the process data that are recommended for developing a PFC measurement strategy, for calculating Tier 3 coefficients and for comparing with other measurement results.
 4. **Sampling Design.** Guidelines for sampling are described.
 5. **PFC Concentration Measurement.** Guidance is provided on proper instrumentation and techniques for measuring PFCs in ducts and rooftop measurements.
 6. **Calculations and Reporting.** Calculations and good practices for reporting data are presented.
 7. **QA/QC.** This section presents the steps that should be taken to assure that the measurement process is in control and instruments and sampling systems are performing as needed to achieve an accurate result.
 8. **Safety.** This section presents the recommended steps and procedures that should be taken to help minimize the risk of injury to measurement staff during the measurements.
 9. **Measurement Frequency and New Measurements.** Guidelines for when new measurements should be made to reassess emissions factors are presented.
- Appendices.** The appendices provide additional information to aid in the measurement process. Included are spreadsheet templates for data collection, calculations and reporting, a list of suppliers of equipment, and guidance for assessing measurement results.

2.0 Background

This section presents an overview of the nature and role of PFCs in climate processes. Sections 2.1 and 2.2 discuss what PFCs are and their climate change impact. Section 2.3 describes how they are produced, in particular, their possible release mechanisms and the potential factors that affect their emission rate.

2.1 *Aluminum Production and PFCs*

2.1.1 **Anode Effects**

Anode effects occur intermittently during aluminum production. They can last from a few seconds to several minutes and are characterized by a sudden increase in cell operating voltage from normal operating levels of 4.2 to 5.0 volts to levels of 25 volts to 50 volts. Anode effects are the primary reason for the elevated cell voltage, and the consequent emission PFCs from the primary aluminum production process.

2.1.2 **Reduction Technologies**

Primary aluminum production facilities are made up of one or more potlines consisting of electrolysis cells operated in series and located either in an end-to-end or side-by-side

arrangement. Electrical current is provided to the potline through rectifiers that convert AC power to DC power.⁶

Two major types of electrolysis processes are used for the production of aluminum: the Söderberg process and the prebake process. These processes are characterized by the type of anode in the cell.

In the older Söderberg process, a single large anode structure is produced from the heat in each electrolysis cell in a continuous process from pitch and coke additions. Alumina is fed into the cell along the side of the structure either by point feeders that incorporate mechanical punches, which break through the crust of frozen bath and alumina cover or, through breaks in the crust formed by wheels or other mechanical means.

The more modern prebake technology involves the production of prebaked anodes in special furnaces outside the electrolysis cell, prior to their use in the electrolysis process. Prebake cell technology is subdivided into several categories depending on the type of alumina feeding mechanism: point fed centre worked (PFPB); bar break center worked (CWPB); side worked (SWPB).

2.1.3 Collection Efficiency and Fugitive Emissions

Primary aluminum production releases small amounts of gaseous hydrogen fluoride and other particulates that must be captured and treated before exhausting to the atmosphere. During normal operations PFPB and CWPB cells typically have gas collection efficiencies greater than 97 percent, while SWPB cells have average collection efficiencies of about 90 percent. Vertical Stud Söderberg cells generally have average collection efficiencies of 80 to 90 percent, unless modified to include covers over the cell sides. Horizontal stud Söderberg cells can have collection efficiencies similar to those for PFPB. Collection efficiency must be considered in for the determination of total PFC emissions. Guidance is provided in Section 5.3.2 for accounting for fugitive emissions.

2.1.4 Mechanism of PFC Release

The specific reaction sequences leading to the formation and release of CF_4 and C_2F_6 are still the subject of study and some differences of scientific opinion. Researchers have proposed that a resistive C-F film might be formed on the anode surface and this film is decomposed to produce the PFC compounds.⁷ ⁸ In any case, previous measurement data have shown that when anode effects occur, both CF_4 and C_2F_6 are immediately released. The release continues until the anode effect is extinguished. The emission rate is highly variable during the anode effect. The emission rate and thus the PFC concentrations rise during the anode effect and then rapidly fall again to atmospheric background levels when the anode effect is extinguished. A PFC measurement strategy must be able to accurately account for these variations.

⁶ For those interested in more details on aluminum reduction technology see J. Thonstad et al., *Aluminium Electrolysis, Fundamentals of the Hall-Heroult Process*, 3rd edition, Aluminium-Verlag, 2001.

⁷ H. Zhu and D. Sadoway, "An Electrochemical Study of Electrode Reactions on Carbon Anodes During Electrolytic Production of Aluminum," *Light Metals* (2000), pp 257 – 263.

⁸ M. Dorren, D. Chin, J. Lee, M. Hyland and B. Welch, "Sulfur and Fluorine Containing Anode Gases Produced During Normal Electrolysis and Approaching an Anode Effect," *Light Metals* (1998), pp 311-316.

3.0 IPCC Three-Tiered Approach

The IPCC has developed and documented guidance on good practices for building an inventory of PFC emissions from aluminum production.⁹ IPCC provides three approaches to estimating greenhouse gases from aluminum production. These approaches are referred to as Tiers 1, 2 and 3.

The highest accuracy results are determined by using the Tier 3 approach. The Tier 3 approach is used to develop a smelter-specific long-term relationship between measured emissions and operating parameters and to apply the relationship to appropriate activity data. The activity data are comprised of aluminum production levels and anode effect data. The anode effect data may be expressed as either anode effect frequency and average anode effect duration or overvoltage for the Rio Tinto Alcan control systems that record potline overvoltage. The procedures described in this document lead to the development of Tier 3 emissions factors used to calculate PFC emissions from the tracking of aluminum production and anode effect process data. The Tier 3 CF₄ emission factors can be estimated based on the two following methods, depending on the facility's process control technology:

- 1) Slope method - anode effect minutes per cell-day, which is obtained from the recorded anode effect minutes for the measurement period divided by the product of the number of cells in the test section and the measurement time in days, or,
- 2) Overvoltage method - potline overvoltage, a parameter related to the excess voltage over normal operating conditions that are recorded for potlines operating with the Rio Tinto Alcan control systems.

Each of these methods is described below.

Slope Method. For this method a linear relationship is established between smelter process data, anode effect minutes per cell-day, and specific CF₄ emissions, i.e., kg CF₄ per metric ton of aluminum. The slope is the parameter which, when multiplied by the anode effect minutes per cell-day, will give the specific PFC emission factor.

Equation 1:

$$EF \text{ (kg CF}_4 \text{ per metric ton Al)} = \text{Slope} \times \text{anode effect minutes/cell-day}$$

Rearranging Equation 1 to the form useful for calculating the facility-specific slope, the following result is obtained.

Equation 2a:

$$CF_4 \text{ Slope} = EF \text{ (kg CF}_4 \text{/metric ton Al)} \div \text{anode effect minutes/cell-day}$$

Overvoltage Method. For this method the anode effect process data for calculating the smelter specific CF₄ emission factor consists of the time-integrated amount of excess voltage resulting from anode effects.

⁹ IPCC, "2006 IPCC Guidelines for National Greenhouse Gas Inventories", Volume 3, Industrial Processes and Product Use, <http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.htm>, 2006.

Equation 3:

$$EF \text{ (kg CF}_4 \text{ per metric ton Al)} = \text{Overvoltage Factor} \times \text{AEO/CE}$$

Where:

Overvoltage Factor = Proportion factor (kg CF₄ per metric ton Al - percent CE per millivolt overvoltage)

AEO = Anode effect overvoltage (millivolts)

CE = Aluminium production current efficiency (percent)

Rearranging in the form to calculate the facility specific AEO factor:

Equation 4:

$$CF_4 \text{ Overvoltage factor, } F_{OV} = EF_{CF_4} \text{ (kg CF}_4 \text{/metric ton Al)} \times \text{CE/AEO}$$

For all facilities, whether using the slope method or overvoltage method, C₂F₆ emission factors are determined as a weight fraction of the CF₄ emission factor. The weight fraction, R_{C₂F₆/CF₄}, is determined from individual facility-specific measurements (per Tier 3 factors) or from the average of measurement factors made from a number of facilities operating with similar technology (per Tier 2 C₂F₆ factors).

Equation 5:

$$C_2F_6 \text{ Weight Fraction} = EF \text{ (kg C}_2F_6 \text{/metric ton Al)} / EF \text{ (kg CF}_4 \text{/metric ton Al)}$$

Equations 1 through 5 form the basis for calculation of the Tier 3 coefficients for calculations of CF₄ and C₂F₆ emissions from smelter process data. These equations are embodied in the worksheets included in Appendix A.

4.0 Process Data Requirements

The objective of the measurement process is to develop the data necessary to calculate Tier 3 coefficients for estimating PFC emissions based on aluminum production data and anode effect data. The collection of accurate process data on anode effects and other facility processes is a key part of the measurement process. This section presents the specific information that should be gathered and summarized prior to initiating measurements.¹⁰ Data on reduction technology, anode effects, and cell ventilation flow rate will be used to develop the sampling and analysis plan. These data will allow estimates of concentration of PFCs in the exhaust ducts and in fugitive emissions to prepare operating standards and to establish optimum calibration ranges for instrumentation. In particular, data are needed for characterizing the following facility properties:

- 4.1 Reduction Technologies;
- 4.2 Anode Effects;
- 4.3 Overvoltage Data;

¹⁰ During planning for the measurements arrangements should be made for the timely collection of the anode effect and other data in the section of cells at which the PFC measurements will be made.

- 4.4 Aluminum Production Data;
- 4.5 Characteristics of Computer Control System, and,
- 4.6 Other Cell Parameters.

4.1 *Reduction Technologies*

The reduction cells on which PFC measurements are being made should be characterized as one of the following types:

- Prebake cell technologies:
 - Center work: 1) point feeders (PFPB); or 2) bar break (CWPB)
 - Side work (SWPB)
- Søderberg technologies:
 - Vertical Stud Søderberg (VSS): 1) normal side break feeding; or 2) upgraded with point feeders
 - Horizontal Stud Søderberg (HSS)

Some primary aluminum production facilities may operate with more than one type of reduction cell at the same site. At such sites, a separate measurement should be made for each type of reduction cell and control system to reflect accurately the emissions of the entire site.

4.2 *Anode Effects*

While anode effects are easily recognized when they occur due to the large increases in cell voltage, important differences exist in the specific definitions of anode effects that should be recorded for the site.¹¹

- **Voltage Criteria.** The specific voltage at which the cells are declared to be on anode effect should be recorded. This voltage is commonly referred to as the “trigger voltage”. Most facilities record the onset of anode effects with computer control systems that scan individual cells at a frequency ranging from fractions of a second to 1 minute or more. Rules are coded into the computer for anode effect detection that includes the voltage above which the cell is declared to be on anode effect. Also, some computer systems may require the initial recording of high voltage to be confirmed before the system

¹¹ While there is no standard definition of anode effects used by all aluminum production facilities, the most often used approach for non-Pechiney technology plants is as follows:

A pot enters anode effect status when the cell voltage exceeds 8.0 volts. The anode effect is considered to be terminated (“killed”) when the voltage falls below 6.0 volts. Anode effect minutes per cell-day (AE-min/cell-day) are the total minutes that the pot is at a voltage greater than 8.0 volts for each full day of operation. After the anode effect is extinguished, a series of anode raises are made until the pot reaches the lower resistance target range. At this time, a counter is started. If an anode effect occurs within 15 minutes of the pot re-entering this target range, it is considered a repeat anode effect, and is not counted as a new anode effect. After this 15-minute period, any anode effects are counted as new.

Anode effect duration recorded by the older Pechiney control computer systems cannot be compared with those of alternative control systems. The newest Pechiney control systems record anode effect duration in both the time above 8 volts and as the total anode effect treatment time.

records an anode effect. Whether the initial time increment is included in the definition of time on anode effect should be recorded.

- **Anode Effect Frequency.** The average anode effect frequency for the reduction line where PFCs are measured should be documented. Additionally, the anode effect frequency for the specific test cells to be measured should be calculated for the measurement period and compared with the historical data. How a new anode effect is distinguished from a continuation of a prior anode effect should be determined and recorded. As noted above, the detection of the onset of an anode effect is unambiguous but some differences exist in the way that anode effects are counted by computer control systems. These site-specific rules for how anode effects are counted should be recorded. The specific rule that determines how the situation is treated when voltage dips to a value less than the trigger value but then at a later time again increases above the anode effect trigger voltage value should be recorded. Typically some time interval is defined during which, if another voltage increase occurs on the same cell, the increase is recorded as a continuation of the prior anode effect rather than the start of a new anode effect.
- **Anode Effect Duration.** Prior to measurements, the average anode effect duration for the reduction line to be measured should be documented. During measurements, the duration of each anode effect and the average anode effect duration in minutes should be determined for the specific group of cells undergoing measurements and compared with the documented average data to ensure measurements represent consistent conditions. The duration of anode effects is typically measured by the computer control system. The computer counts the number of scan cycles when the cell's voltage is above the trigger level for each anode effect. The trigger level should be recorded and reported with anode effect duration data. The number of cycles for which an elevated voltage is detected is then multiplied by the scan cycle time to obtain the duration of the anode effect. If another definition of anode effect duration is used the details of the definition should be reported.
- **Distribution of Duration of Anode Effects.** In addition to the average anode effect duration, the statistical distribution of the duration of individual anode effect events for the most recent month for which data are available should be obtained and documented for the potline(s) for which the calculated emission coefficient is to apply. The distribution of anode effect durations recorded during the measurement should be compared with the most recent month data as a process check. Also, changes in the long term anode effect duration distribution should trigger consideration of a new measurement (see Section 10, Measurement Frequency and New Measurements).
- **Anode Effect Cause.** Many facilities record information about each anode effect, such as whether the event occurred during tapping, anode set, or resistance tracking, and, whether the anode effect was terminated by the computer control system or required a manual intervention. These data should be recorded if available.

4.3 Overvoltage Data

If an overvoltage coefficient is to be calculated, then, average overvoltage data should be obtained prior to conducting measurements for the reduction lines to be measured. During

measurements, overvoltage data should be obtained and recorded for the specific group of cells where CF₄ and C₂F₆ are being measured.

The overvoltage data are the integral (i.e. sum) of the product of time and voltage above the target operating voltage (corresponding to the target resistance), divided by the time over which the data are collected (e.g. hour, shift, day, month).

Equation 6:

$$AEO = \frac{\int_{t_1}^{t_2} (V_t - V_{trigger}) \Delta t}{\text{Number of cells} \times (t_2 - t_1)}$$

Where:

- AEO = Overvoltage (Volts)
- t₁ and t₂ = Times at the beginning and end of the time period for calculating overvoltage (seconds)
- V_t and V_{trigger} = Instantaneous cell voltage and the anode effect trigger voltage for the cell on anode effect (V)
- Δt = Time interval between successive scan cycles of each cell
- Number of cells = Number of cells in the section being considered

During each anode effect, the cell overvoltage recorded by the control system at each scan cycle is multiplied by the scan cycle time (in seconds). The total of these volt-seconds recorded for the group of cells being measured is then divided by the number of cells and the time (in seconds) over which the data are collected to calculate the overvoltage data for the group of cells. Since time is included in both numerator (as seconds) and denominator (as days), the data in the expression can be reduced to units of voltage. These data, expressed in millivolts, are the anode effect overvoltage (AEO) data that are used in equation 6 to calculate the Overvoltage factor for CF₄ emissions. Any deviation from this definition should be reported, such as “algebraic” overvoltage,¹² voltage marking the end of anode effect, or if the target operating voltage is replaced by a fixed conventional voltage to account for overvoltage.

4.4 Aluminum Production Data

The average rate average of aluminum (Al) production should be obtained and recorded for purposes of normalizing the time rate of emissions of CF₄ and C₂F₆ to obtain emission factors for kg CF₄/metric ton Al and kg C₂F₆/metric ton Al. The actual aluminum production, as measured using tap weights, should be compared to the calculated value, as calculated using line current and current efficiency:

- **Tap Weights.** The time rate of aluminum production should be obtained and recorded from the average of metric tons Al per cell-day over the past one month period from production tap weight data.

¹² “Algebraic” refers to a method of overvoltage accounting where voltages under target operating voltage result in a discount on overvoltage.

- **Line Current and Current Efficiency.** The average line current in kiloamperes and current efficiency for aluminum production should be obtained from location staff and recorded for the potline to which the measurements apply. The expected average production rate for primary aluminium should be calculated and recorded as a comparison with the value obtained from tap weight data, according to the following equation:

Equation 7:

$$\text{Aluminum Production (metric ton Al/cell-day)} = 0.008058 \text{ (metric ton Al/(kA-cell-day))} \times I \times CE$$

Where:

I = Line current (kiloamperes)

CE = Current efficiency for aluminum production (as a decimal fraction)

From Faradays Law, 0.008058 metric tons of Al are produced per kA-cell-day at 100 percent current efficiency.

If the result from this calculation differs by more than 5 percent from the previous months tap weight data as collected in the smelter data sheet, Appendix A, both pieces of data should be examined to resolve the conflict.

4.5 Characteristics of Computer Control System

Information should be recorded about the process computer control system. Section 4.3 defines some of the characteristics of the computer control system. The additional key information needed to characterize the system is the scan rate and what steps are taken to automatically kill an anode effect once the anode effect is initiated.

The scan rate is the frequency at which each cell in the potline is interrogated and cell voltage data collected. The scan rate represents the upper limit of temporal resolution of anode effect data. When the scan rate is very fast, many cycles per second, a large amount of data are generated and some amount of time averaging is done on the data before storing in the computer data recording system.

The average efficiency of the computer system in killing anode effects should be recorded. This parameter is typically referred to as “percent manual kills” or “percent impossible.” The percentage of manual kills impacts overall PFC emissions in that the duration of these anode effects is typically relatively long and manual intervention by inserting a wood pole into the cell is necessary to kill the anode effect. Fewer mitigation options are available for Söderberg cells, however, in some Söderberg cells, compressed air is injected under the anode on computer detection of an anode effect. If anode effect kill mitigation is employed at a Söderberg facility then it should be noted.

4.6 Other Cell Characteristics

Other cell characteristics, including dimensions of anodes and average bath volume which may contribute to the voltage behavior of the cell on anode effect, should be noted to help put the measurement results in context.

5.0 Sampling Design

Care should be exercised to ensure that PFC sampling fairly represents the long-term operations of the potline. Also, attention should be given to proper measurement and treatment 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. This section presents the seven key factors for defining the sampling design:

- 5.1 Reflection of “Normal” Conditions;
- 5.2 Sampling Configuration;
- 5.3 Sampling Locations;
- 5.4 Flow Homogeneity Requirements;
- 5.5 Sampling Time;
- 5.6 Duct Flow Measurement; and
- 5.7 Potroom Rooftop Flow.

5.1 Reflection of “Normal” Conditions

Before considering measurement of PFCs for the purpose of establishing IPCC Tier 3 equation coefficients the potline should be operating in a control condition with respect to those process variables that would affect the Tier 3 coefficients. Key process parameters that should be stable include bath chemistry, distribution of anode effect durations, anode effect termination algorithm, percentage manual terminations, and cell control and feed strategy. The start up of a new cell, while a normal event in the long-term operation of a potline, should be avoided if possible during the sampling for determination of emissions factors. Prior work has shown that the impact of new cell start-ups on overall emissions is negligible unless there is a major restart campaign.¹³ Other events that would result in atypical operation of the line should be avoided during the measurement campaign. All the cells on which PFC 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 (see Section 10.0, Measurement Frequency and New Measurements).

A histogram of anode effect duration should be prepared and compared with the histogram of the previous month’s data to assure that the test period is representative of longer-term performance. Similarly, a comparison should be made on the percent of manual kills of anode effects. In particular, some PFPB facilities have low anode effect frequencies where slope or overvoltage coefficients may have to be based on a limited number of anode effects. For these facilities special care must be taken to ensure that anode effect measurements are representative. For example, care should be taken to account for any reduction in collection efficiency that may result from opening cell hoods during anode effect termination.¹⁴

¹³ Guy Bouchard, Jens Kallmeyer, Alton Tabereaux and Jerry Marks, “PFC Emissions Measurements from Canadian Primary Aluminum Production,” *Light Metals* (2001), 283 – 288.

¹⁴ When manual intervention is required to kill anode effects typically potroom staff will be alerted and will proceed to the cell on anode effect within a period of about two minutes. The anode effect will be treated by “green poling” after removing one or more of the cell covers, or, by opening the cell end door. This action will impact the exhaust collection efficiency and may result in significant losses of PFC gases from the exhaust system. There have been no quantitative measurements of the reduction in collection efficiency during green poling; however, specific

5.2 Sampling Configuration

Several sampling designs have been tested and found effective in measuring PFCs in exhaust ducts and for sampling fugitive PFC emissions. These designs serve as examples for assembling a sampling system. The specific system of pumps, sample lines, filters, scrubbers and other gas transfer equipment depends on the needs of the site and the sampling requirements. Summarized below are two approaches that have proven effective for measuring PFCs.

- **For sampling PFCs in smelter exhaust ducts.** The exhaust gas intake is first filtered through a sintered stainless steel filter on the end of a length of stainless steel tubing inserted through a sample port in the duct. The sample is drawn continuously out of the exhaust duct by use of sampling pumps or a gas eductor through the stainless steel sampling probe, then transferring through a Teflon or polyethylene sample transfer line, through a dust filter and any needed sample stream conditioning treatment required. The flow is directed to the at-line analyzer or, alternatively, to the sample container if a time average sample is being collected.
- **For sampling PFCs in the potroom roof and background emissions.** The intake consists of a polypropylene or stainless steel particulate filter on a Teflon or polyethylene sample transfer line connected to a low flow rate sampling pump, which draws the gas into a gas sample bag or sorbent column at a constant flow rate.

5.3 PFC Sampling Locations

Safe access should be a key criterion for all sampling operations. PFC sampling locations in the fume collection ducts should be chosen to ensure that the gas sampled is homogenous and fully representative of the cells for which anode effect data are being collected. Below, the key considerations are described for the three sampling locations necessary for measurements:

- 5.3.1 Duct Locations;
- 5.3.2 Accounting for Fugitive Emissions; and
- 5.3.3 Background Sampling Locations.

5.3.1 Duct Locations

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 accurately measurable with the chosen instrumentation. Ventilation gases from all the other cells in the section being measured act to dilute emissions resulting from an anode effect in one cell. By combining knowledge of the dynamic response range of the measurement instrumentation and estimates of the concentration of PFC gases to be

measurements of the impact on collection efficiency and associated adjustments can be made if significant. For example, any reduction in collection efficiency during green poling can be assessed by making single cell measurements of the reduction in carbon dioxide emissions. The change in collection efficiency can then be calculated from the reduction in carbon dioxide collected by the exhaust during the time the cell is open. The feasibility of making carbon dioxide measurements on single cells is limited in some of the most modern cell ventilation designs due to multiple duct configurations. An example of the impact of fugitive emissions can be found in the reference, C. Martin and E. Couzinie, "PFC Emissions Measurement from Aluminium Pechiney Smelters," *Light Metals* (2003), pp 233 – 240.

expected as described below, sampling locations can be properly selected. Another important factor in the choice of sampling location is accessibility, since periodic access is required to check duct flow rate and to do routine checks of the sample probe. Experience has shown that the optimum sampling location is normally at the exhaust stack downstream of gas treatment facilities. This location gives the maximum number of cells that can be sampled for a potline and is typically the most homogenous gas stream available, since it is well downstream of any cell inlet, combines the exhausts of any auxiliary ducting from booster fans and has been through the exhaust fans. However, CF₄ and C₂F₆ will be at their lowest concentrations at this point because they have been diluted by the exhaust of all the cells that are not on anode effect; consequently, the sensitivity of the measurement instrument should be checked to ensure that it is adequate for accurate measurement at this location.¹⁵ Calculations of expected rooftop average PFC concentrations can be made from the average collection efficiency, the calculated PFC emissions escaping the collection system and the measured detection limits of the instrumentation.

Prior to beginning sampling and measurements, CF₄ and C₂F₆ concentrations should be estimated to establish the instrument measurement and calibration range. Appendix A contains a spreadsheet file for estimating approximate PFC concentrations during anode effects, and, provides guidance for optimum sampling times for time average bag sampling. In general two measurement techniques are available for estimating CF₄ concentrations:

- **At-line measurements.** Estimates of duct concentrations of CF₄ in near real time measurements can be made for an anode effect by applying calculations based on IPCC recommended Tier 2 values for the slope method for CF₄.

Equation 8:

$$CF_4 \text{ Concentration (ppmv)} = S \times K_S \times I \times CE / (f \times N)$$

Where:

- S = IPCC recommended Tier 2 slope values for each reduction cell technology type (kg CF₄/metric ton Al)/(anode effect minutes/cell-day)
- K_S = Constant (µl CF₄-metric ton Al)/(kg CF₄-kA-cell-day) = 2.05 x 10⁶
- I = Line current (kA)
- CE = Current efficiency for aluminum production (fraction)
- f = Ventilation flow rate per cell at 0°C and 1 atm (liters/minute-cell)
- N = Number of cells in test section of cells to be measured (cells)

Or, for facilities operating with overvoltage:

Equation 9:

$$CF_4 \text{ Concentration (ppmv)} = F_{OV} \times K \times AEO \times I / (f \times N \times AEF \times D)$$

¹⁵ In some instances where the anode effect frequency may be high there may be many overlapping anode effects making it difficult to correlate anode effect process data, duration or overvoltage, with the PFC emissions from individual anode effects. Individual anode effect information is useful in characterizing the dataset. In particular, the sensitivity of the calculated slope or overvoltage parameter to changes in anode effect duration can be analyzed, as well as examination for data outliers. However, it is not essential in calculating the slope or overvoltage coefficients.

Where:

F_{OV} = IPCC recommended Tier 2 Overvoltage Factor (kg CF₄-% CE/metric ton Al-mV)

AEO = Overvoltage (mV)

K_{OV} = Constant ($\mu\text{l CF}_4\text{-metric ton Al}/(\text{kg CF}_4\text{-kA-% CE}) = 2.05 \times 10^4$)

I = Line current (kA)

f = Ventilation flow rate per cell at 0°C and 1 atm (liters/minute-cell)

N = Number of cells in test section of cells to be measured(cells)

AEF = Anode effect frequency (Anode effects per cell day)

D = Average duration of anode effect (minutes > 8 Volts)

- **Time average sampling into bags.** For time average samples for duct samples approximate long term average concentration of CF₄ should be estimated according to the following equation.

Equation 10:

$$CF_4 \text{ Concentration (ppmv)} = S \times K_S \times I \times D \times CE / (f \times N \times t)$$

Where:

S, K_S, I, f and N = As defined for Equation 7.

t = Sampling period duration (minutes)

D = Duration of anode effects expected in the sampling period (minutes)

Or, for facilities operating with overvoltage, the long term average concentration for bag sampling is:

Equation 11:

$$CF_4 \text{ Concentration (ppmv)} = F_{OV} \times K_{OV} \times I \times AEO \times CE / (f \times N)$$

Where:

F_{OV} = IPCC recommended Tier 2 Overvoltage Factor (kg CF₄- % CE/metric ton Al-mV)

AEO =Overvoltage (mV)

K_{OV} = Constant ($\mu\text{l CF}_4\text{-metric ton Al}/(\text{kg CF}_4\text{-kA-% CE}) = 14.2$)

N = Number of cells in test section of cells to be measured cells)

f = Ventilation flow rate per cell at 0°C and 1 atm (liters/minute-cell)

5.3.2 Accounting for Fugitive Emissions

Fugitive PFC emissions, those not collected in the cell exhaust duct and escaping through the potroom rooftop, should be accounted for and then added to those PFC emissions measured in the exhaust duct. The concentrations of CF₄ and C₂F₆ exiting the rooftop are very dilute, <10 ppbv on average, due to the large potroom ventilation flow rate. Several acceptable options are described here to account for fugitive emissions and the specific adjustment method should depend on the fugitive fraction and measurement system capability.

Collection fraction equal to or greater than 90%: When collection efficiency is 90% or greater, the total CF₄ and C₂F₆ emissions can be calculated by dividing the emission rate measured in the exhaust duct by the collection fraction. For example,

Total kg CF₄/t Al = kg CF₄ duct/Collection Fraction

Collection fraction less than 90%: When collection efficiency is less than 90% as can be encountered for PFC measurements at some SWPB, VSS and HSS facilities, extra attention should be given to the accurate accounting for fugitive emissions.

If measurement methods are available with adequate sensitivity to make an accurate measurement of CF₄ exiting the rooftop, a direct measurement of CF₄ emissions can be made and the measured fugitive emissions then added to those measured in the exhaust duct in order to calculate total CF₄ emissions. Fugitive C₂F₆ emissions are then calculated by multiplying the CF₄ fugitive emissions by the measured weight fraction, F_{C₂F₆/CF₄}, measured in the exhaust duct. Rooftop sampling locations should be chosen for good accessibility, safety and availability of any needed services. Samples of fugitive emissions from potroom roofs should be taken from EPA Method 14 or similar available sampling systems if that system is available.¹⁶ EPA Method 14 provides for sampling a representative section of the rooftop flow through a series of funnel shaped intakes. These sample intakes are joined in a manifold and then are brought to ground level through a duct operated at a slightly negative pressure.

If no such sampling system is in place, sampling locations that represent the average flow from the rooftop should be selected based on discussions with the smelter contact person. Fugitive samples can be collected by pumping a constant small flow of gas into appropriate sample bags to develop a time average composite sample. A minimum of three point locations should be chosen to reflect the overall average flow out of the potroom.

If measurement methodology is not available for accurately measuring CF₄ exiting the rooftop then fugitive emissions should be calculated as per the methodology for a collection fraction is equal to or greater than 90%. Whether fugitive emissions are measured or calculated the associated uncertainty in the values should be calculated and reflected in the overall Tier 3 coefficient uncertainty.

5.3.3 Background Sampling Locations

A background sample should be taken from an area adjacent to the potroom where measurements are being made in a similar manner to the rooftop fugitive sample. The purpose of the sample is to test for any interference that might contribute to the analyte signal. Background CF₄ and C₂F₆ levels should be insignificant compared to average concentrations in the fume ducts or to fugitive emissions for those facilities where fugitive emissions are measured. While some potential exists for back ingestion of PFC emissions from the fume treatment facility, dilution of these emissions should make these concentrations insignificant compared with primary emissions from potrooms.

¹⁶ U.S. EPA, *Environmental Protection Agency Method, 40 CFR, Ch. 1, Pt. 60, App.A, Method 14*, 1993, <http://www.epa.gov/ttn/emc/promgate.html>. This method describes a rooftop sampling system that draws an air sample from the roof monitor to ground level.

5.4 Flow Homogeneity Requirements

For accurate calculation of Tier 3 emission coefficients, a direct correlation of anode effect data with the resulting emissions measured in the exhaust collection duct is essential. The measured concentrations of CF_4 and C_2F_6 in the duct must be representative of the entire flow in the duct location where sampling takes place. Mixing must be complete in the duct at the sampling location. The optimum location for sampling in the duct system is downstream of the gas treatment facility, normally at the exhaust stack just before release to the atmosphere. At this point the gases have been well mixed having passed through the fans exhausting the duct system. Also, because this point is evaluated for other environmentally important emissions, sampling ports are normally available as is access by ladder or stairs. If this sampling point is not suitable, an alternative is to sample at the inlet to the gas treatment facility. This point is typically well downstream from the location of any cell inlet to the duct allowing time for good mixing. This sampling location is also normally easily accessible and sampling ports are available because of other plant sampling needs. When neither of these sampling locations is available care must be exercised to avoid errors due to incomplete mixing in the exhaust duct from which the sample is extracted. Incomplete mixing can occur where two duct sections are joined and the flow streams can remain segregated for distances of 10 meters or more. In cases where segregation of the gas stream is likely the homogeneity of gas composition should be evaluated. Where segregation is found in the gas stream an alternate sampling location should be selected.

5.4.1 Evaluating Homogeneity of Duct Flows

Potroom fume collection systems are typically designed to draw fumes from each cell into a duct that merges into a header, which collects fumes from a group of cells. These headers are then merged with other ducts that may in turn be further merged to collect fumes for gas fume treatment. Experience has shown that gas flows may remain segregated for some distance 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. When these concentrations are applied to the full flow in the duct, erroneous emission fluxes will be recorded. To avoid such errors a new sampling location should be chosen whenever non-homogeneity of greater than 10 percent is measured across the duct cross section.

5.4.2 Testing for Homogeneity

When sampling at locations other than the gas treatment facility stack outlet or, the gas treatment inlet and where the distance from the last cell inlet is less than 20 meters from the sample extraction point, segregation of the gas composition in the duct may be an issue and the homogeneity of PFC concentration across the duct cross section should be tested to confirm the viability of the sampling point. The homogeneity test is accomplished by injecting a small constant flow of a tracer gas¹⁷ into the exhaust duct of one of the reduction cells and then

¹⁷ 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 in a number of applications because it has good sensitivity for infrared measurements, is not normally present in the gas stream, and is relatively stable at the temperature encountered in the fume duct system. However, SF_6 is also a strong greenhouse gas with a long atmospheric lifetime and should be avoided if another tracer can be successfully used. Another tracer gas with much

monitoring the concentration of the tracer at the candidate sampling point in the main duct. A stainless steel probe is inserted into the duct and the concentration of the tracer is measured at five equally spaced points across the duct cross section. An alternate approach is to inject tracer gases into the exhaust ducts of cells that represent the greatest possibility for segregation and measure the tracer concentrations at a fixed sampling point. The concentrations should not vary by more than 10 percent at any of the sampling points. If the variation is greater than 10 percent another sampling location should be tested.

5.5 Sampling Time

The sampling strategy should allow for a good statistical sampling of long-term anode effect frequency and anode effect duration distribution. Because anode effects of similar duration have high variability in emissions of CF_4 and C_2F_6 the sampling strategy needs to give a robust average value of emission coefficient by reflecting all aspects of the aluminum production process. Consequently, the duration of sampling during all the cycles of smelter operation needs to be addressed in the sampling strategy. Each of these factors is described below.

- **Sampling Time.** A running average for Slope or Overvoltage coefficient and weight ratio for C_2F_6 to, CF_4 should be calculated after each eight to twelve hour sampling period as new measurement data is being collected. Sampling should continue until the running average of the Slope or Overvoltage coefficient 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. For the most modern smelters operating with anode effect frequencies at or below 0.1 anode effects per cell-day, the 10 percent variability standard may be difficult to achieve. For these high performing locations a long term sampling campaign of weeks or months may be necessary to reach the 10 percent variation criterion noted above. For these high performing facilities it is particularly important to carefully evaluate and report the uncertainty in the calculated Tier 3 coefficients. At locations with very low anode effect frequency, deliberate feed interruptions may provide additional measurement data; however, care should be exercised in evaluating whether these induced anode effects are representative of those that occur normally.
- **Reflection of Smelter Production Cycles.** Sampling should include all the normal cycles of smelter operation (i.e. tapping, tracking, feeding and anode changing). Normal smelter operations involve repeating several different operational steps during which time cells are tapped of aluminum and fed under predetermined schedules. In addition, anodes are changed on a specific schedule. Finally, there is a time period when cells are allowed to electrolyze the available alumina in the bath without new additions to confirm whether the resistance is decreasing or increasing over time (“tracking”). Incorporating all the production cycles into the sampling period is consistent with the sampling time requirements described above.

lower climate impact than SF_6 is Tetrafluoroethane-1,1,1,2 (R134A), $\text{C}_2\text{H}_2\text{F}_4$ which may be useful for some applications.

5.6 Duct Flow Measurement

The gas flow velocity in the duct where PFCs are sampled should be measured at time intervals sufficient to accurately convert CF₄ and C₂F₆ concentration values into mass emission rates. The flow rate should be measured by either one of the methods described below. Temperature and pressure in the duct may need to be measured so that the mass flow rate can be calculated.

- **Pitot Tube Method.** The volumetric flow rate can be determined using the methodology described in EPA Method 1 – Sample and Velocity Traverses for Stationary Sources.¹⁸
- **Tracer Gas Injection Method.**¹⁹ Alternatively, the volumetric flow rate can be assessed by injecting a constant known amount of a tracer gas into the duct upstream of the sampling point. The concentration of the tracer is then measured at the sampling point. From the dilution factor the volumetric flow rate can be calculated as follows:

Equation 12:

$$\text{Duct flow rate (l/min at 0 °C and 1 atm)} = I \times 10^3 / C$$

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)

10³ = µl/ml

The tracer method has an advantage of being capable of assessing short-term variation in duct flow rate. The method is particularly advantageous when instruments capable of simultaneously measuring the tracer gas and the PFC components are in use.

5.7 Potroom Rooftop Flow

When duct collection efficiency is less than 90 percent, special attention is needed to account for emissions escaping the exhaust collection system and exiting the rooftop. These emissions can be sampled concurrent with duct sampling. While no specific requirement exists to isolate the rooftop emissions of the particular cells for which measurements in the fume duct are made, fugitive emissions should be measured in the specific potroom where duct measurements are made.²⁰

¹⁸ U.S. EPA, *Environmental Protection Agency Method 1, Pt. 60, App. A, Method 1, Sample and Velocity Traverses For Stationary Sources*, 1993, <http://www.epa.gov/ttn/emc/promgate.html>

¹⁹ For measurements using infrared spectroscopy the measurement of gaseous carbon compounds, over 99 percent of which consist of carbon dioxide and carbon monoxide, can serve as very useful tracer gases. The duct flow rate can be calculated with each measurement cycle by calculating the dilution of the carbon gases, resulting from the reaction of the carbon anode at a rate that is carefully monitored in almost all aluminum production plants in the parameter “net anode consumption.” For best results net anode consumption should be corrected for non-carbon components to calculate the net carbon consumption rate.

²⁰ In some measurement applications, duct emissions result from cells in two different potrooms. If operational procedures are similar in both potrooms, fugitive measurement in one of the potrooms is adequate. The approach here is to measure duct and fugitive specific emissions separately and then add the two specific emissions to arrive at the total specific emissions. The main requirement for the efficacy of this approach is that the factors affecting overall PFC emissions and capture efficiency in the cells where duct PFCs are measured are similar to those in the potroom where fugitives are measured.

During rooftop sampling ventilation rates (volume flows out of the roof) should be calculated using whatever flow measurement system is in place and routinely used by the smelter personnel. There can be substantial variability in rooftop flow rate with the diurnal cycle or changes in wind patterns around the potroom. Variable rooftop flow is most significant when potroom floor and basement airflow is reduced, such as occurs during winter months at smelters in cold climates, as well as smelters with wide roof monitors. Consequently, the potroom rooftop flow should reflect the conditions during the actual measurement period. These measured flows should then be applied to the specific samples taken in the rooftop location to calculate PFC fugitive emissions for the sampling period.

Time-averaged samples should be drawn from the chosen sampling locations using constant flow pumps. The samples should be collected into gasbags over periods of time that account for the operating cycle of the potroom. The exhaust gas should be pumped at a constant rate to collect an adequate amount of gas for the analysis to be made. For example, about 30 to 40 cc/min is required to collect about 20 ± 2 liters of sample over an 8 to 12 hour period. These samples should be taken concurrently with the continuous monitoring of the duct gas, and labeled with the date and time of collection.

Temperature and atmospheric pressure should be recorded so that rooftop flows can be reduced to standard conditions for calculation of PFC flux rates.

6.0 PFC Concentration Measurement

Two different approaches can be used to measure PFC concentrations. Measurement can be made to determine CF_4 and C_2F_6 concentrations in sample bags or from sorbent columns²¹ that are collected at the measurement site over some extended sampling period. The measurement of the PFC concentration in the bag samples or sorbent columns can be made either at the test site or transported to a laboratory for measurement. Alternatively CF_4 and C_2F_6 concentrations can be measured at the site using at-line instruments measuring PFC concentrations in near real time as anode effects occur. Either approach, when implemented according to the good measurement practices described here, results in an accurate Tier 3 measurement coefficient. Each approach has both advantages and disadvantages as discussed below.

Typically the measurement of time average bag or sorbent column samples in the laboratory or by portable equipment transported to the test site is a less costly approach. The time average bag or sorbent column techniques also allow for multiple samples to be taken simultaneously from a number of points, such as from multiple potlines in a facility or from multiple rooftop points. If smelter trained in sampling and gas volume measurement are available, the samples can be taken and forwarded to a laboratory for measurement. The immediate feedback of measurements conducted at the production line in near real time provides the opportunity to adjust measurement and sampling strategy if unexpected problems are encountered. The near real time continuous measurement also allows the collection of data on emissions from individual anode effects. This data is useful for quality control purposes. The final choice of method should depend on what measurement equipment is available and the experience level of measurement staff.

²¹ N. Sauret-Szczepanski, G. Patry, J. Ross, G. Potvin, S. Gauthier and C. Munger, "Development of a Sorbent Adsorption/Desorption and GC/MS Method for the Determination of Perfluorocompounds (CF_4 and C_2F_6) Emitted from Aluminum Smelters," Aluminum 2006, 45th Annual Conference of Metallurgists of CIM, 2006, pp 53 – 65.

6.1 Standards

Standards containing CF_4 and C_2F_6 should be prepared that cover the full range of concentration expected to be encountered in the measurements. Working standards can be purchased from commercial gas suppliers and should be traceable to or certified by the U.S. National Institute of Standards and Technology (NIST), or a comparable national standard setting organization.

6.2 Instruments for Laboratory Based Measurement Methods

If a laboratory based measurement approach is chosen, either gas chromatography with mass spectrometry detection (GC/MS) or Fourier Transform Infrared Spectrometry (FTIR) can be used for measurement of CF_4 and C_2F_6 from exhaust duct samples. Each of these approaches is described below.

6.2.1 GC/MS

GC/MS analysis results are free of interference from other gas species that accompany the PFCs. The measurement may be made directly on gasbag samples or by desorbing the PFC components after time average sampling onto sorbent columns. Using direct sampling of gas samples in bags or metal canisters separation of CF_4 and C_2F_6 can be accomplished using liquid nitrogen to cool the GC column to -40°C . The chromatography takes place on a stainless steel (3.2 mm x 3.7 m) Alumina 5 Å 80/100 mesh column or the performance equivalent. The temperature is then ramped from -40°C to $+40^\circ\text{C}$ to elute reduction cell exhaust gas components. Carbon dioxide and traces of water are eluted after running a series of samples by ramping to high temperature. When sorbent columns are used for PFC samples are captured on Carboxen 1000 after conditioning in flowing nitrogen for twenty four hours. The PFC compounds are thermally desorbed with nitrogen. The gas chromatograph is equipped with a gas valve injector fitted with a 250 μL loop and the oven is operated isothermally at 30°C . The mass selective detector is operated in the single ion monitoring mode at m/z 69 which is characteristic of both PFC components. Working standards should be prepared by diluting more concentrated CF_4 and C_2F_6 standards in nitrogen. Gas volumes should be measured with gas-tight syringes. Using fifty microliter injections of both samples and standards, detection limits of 0.05 ppmv and 0.04 ppmv CF_4 and C_2F_6 , respectively, can be achieved. Using the sorbent columns detection limits of 9 ppbv for CF_4 and 0.6 ppbv for C_2F_6 have been validated. Detection limits can be improved with simple modification of desorption parameters if desired.

6.2.2 FTIR

CF_4 and C_2F_6 contents should be measured in a 10-meter path length gas cell. The spectrometer should be calibrated with gas standards certified by or directly traceable to the U.S. National Institute for Standards Technology (NIST), or a comparable national standard setting organization. The smelter exhaust gas sample is allowed to fill an evacuated FTIR gas cell to atmospheric pressure. Alternatively, if the volume of sample gas is adequate, the sample can be pumped through the cell. If desired, the sample can be treated to remove components which might result in spectral interference or damage to the gas cell. The sample absorption spectrum

is recorded at a suitable resolution²² using a HgCdTe (MCT) detector cooled with liquid nitrogen or a thermo-electrical cooler. The absorptions at the characteristic wavelengths for CF₄ and C₂F₆ are compared to those of standards measured in a similar manner. Detection limits as low as 0.7 ppbv CF₄ and 1.1 ppbv C₂F₆ have been measured.

6.3 Instruments for Field Measurement Methods

The mass spectrometer, tunable diode laser absorption spectrometer, photoacoustic spectrometer, and the FTIR spectrometer are all commercially available instruments suitable for measuring PFCs in exhaust duct samples at-line at primary aluminum production sites. Each of these methods is summarized below:

- **Mass spectrometer.** The process mass spectrometer provides a near real time measurement of both CF₄ and C₂F₆, as well as several other gas sample components if desired. The detection of the PFC gases is without any serious interference and the sensitivity of the instrument is adequate for the range of concentrations expected for duct measurements. The instrument must be calibrated in place, prior to the start of PFC monitoring. The detection limit for PFC compounds is typically about 0.1 ppm so there is not adequate sensitivity for direct measurement of fugitive PFC emissions and an alternative strategy must be used when measurements of fugitives are required. While the mass spectrometer has demonstrated good performance in the relatively strong magnetic fields common around smelter facilities, it is desirable to position the instrument in a location where magnetic fields are relatively invariant, since strong, fluctuating magnetic fields can affect the instrument's response. This equipment is relatively heavy and requires a mobile truck to transport to the measurement location in the facility.
- **Tunable Diode Laser Absorption Spectrometer (TDLAS).** TDLAS is an infrared absorption technique that uses a diode laser to achieve a very narrow emission source bandwidth. As a result, the specificity of the technique is very good. The sensitivity is also excellent and the instrument is capable of direct measurement of both PFC gas components in electrolytic cell exhaust ducts. It has not been applied to fugitive gas measurements. Consequently, if fugitives are to be measured, laboratory analysis of collected time average samples, or open path methodology using FTIR techniques would provide a viable strategy. The TDLAS unit as used for previous PFC measurements is relatively large. A mobile laboratory or trailer is needed to transport the instrument and ancillary sampling equipment from site to site. The equipment as used for past PFC measurements, is not broadly commercially available, is relatively expensive, is specialized and requires experienced specialists to operate it. A newer, lower cost TDLAS instrument has been developed for the measurement of CF₄, however, the instrument has not yet been field-tested.²³

²² Spectral interferences are best avoided by use of operating resolutions of 1 cm⁻¹ or better; however, the measurement can be made using a lower resolution when adequate corrections are made for spectral interferences arising from other components of the exhaust gas stream.

²³ H.A. Gamble, D.R. Karecki, G.I. Macka and H.I. Schiff, "A Streamlined, Portable Mid-IR TDL Based System for On-site Monitoring Of PFCs From Potroom Exhaust Ducts," *Light Metals* (2003), pp 215 – 220, 2003.

- Photoacoustic Spectrometer (PAS).** The PAS is a filter type infrared spectrometer that uses a sensitive microphone as a detector to measure changes in absorption of infrared energy. The instrument is quite sensitive for the PFC gas components; however, interference can occur from any water, sulfur dioxide or methane accompanying the PFC gases. The sample must be conditioned to minimize or remove these potential interferences prior to measurement. Scrubbers containing sodium carbonate or Ascarite can remove hydrogen fluoride and sulfur dioxide. Water vapor is removed by passing the sample stream through a copper tube at dry ice temperature or by using a commercially available drying compound. The instrument calculation software also allows for compensation for limited quantities of interferences by measuring interfering compounds at alternate wavelengths. The PAS does not sample the gas stream continuously as do the other instrument methods described here. Instead the instrument operates in a sequential cyclic analysis mode with a new sample introduced to the analyzer detector on a frequency of once each three to five minutes. The sampling cycle is typically about 15 seconds of this total three to five minute cycle. Accommodation must be made for the substantial dead time of the basic instrument sampling system to prevent bias in results. Collection of time average samples in canisters or sample bags and subsequent analysis with the PAS is an effective approach to overcome the dead time limitation. The instrument is the most portable of the instruments described here weighing approximately 10 kg and is easily operated by staff with a basic knowledge of measurement science.
- FTIR.** The FTIR spectrometer has been used in an open path mode for fugitive emission PFC measurements at aluminum smelters²⁴ and has been used in the extractive mode for PFCs²⁵ and other field analysis applications.²⁶ There are a number of advantages in using FTIR including the ability to measure other components of interest in the gas stream and the ability to post-process the spectral data. As with some of the other methods, potential problems from overlap of interfering spectral bands must be overcome through calibration procedures or spectral stripping algorithms.

7.0 Calculations

This section presents the approach for using the measurement data to estimate emission coefficients. In particular, equations are provided for calculating specific PFC emission factors as kg CF₄ and kg C₂F₆ per metric ton aluminum produced. In addition, the CF₄ slope is computed as well as the overvoltage factors for facilities where overvoltage is recorded. The weight ratio of C₂F₆ to CF₄ is calculated from the measurement data. The spreadsheets included in Appendix A, Data Collection, Calculations, and Reporting Template, have the calculations embedded in them.

²⁴ H.A. Gamble, G.I. Mackay, D.R. Karecki, J.T. Pisano and H.I. Schiff, "Development of a TDLAS Based Method for Monitoring Perfluorocarbon Production During the Aluminum Smelting Process," *Light Metals* (2001), 275 – 281, 2001.

²⁵ N.R. Dando, "In-Plant PFC Monitoring: Technology Options and Performance Concerns," *Light Metals* (2003), pp 205 – 210, 2003.

²⁶ U.S. EPA, *Environmental Protection Agency Test Method 320, 40 CFR Part 63, Appendix A, Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Infrared (FTIR) Spectroscopy*, <http://www.epa.gov/ttnemc01/promgate/m-320.wpd>.

7.1 Option A: Calculating Emission Factors Based on Sampling into Bags or Onto Sorbent Columns for Measurement

This section presents equations for calculating emissions for CF₄ and C₂F₆ 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 C₂F₆ to CF₄. 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.

Step 1: Calculate total gas flows for the sampling period for each duct sampling location and for potroom 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 (m³/h at 0°C and 1 atm)
- V = Average gas velocity (m/s)
- S = Duct cross-sectional area (m²)
- T = Duct temperature (°C)
- P = Duct pressure (mm Hg)
- 273 = Addition factor converting °C to °K
- 3600 = Factor converting hours to seconds (3600 s/hr)
- 760 = Atmospheric pressure (mm Hg)

Calculate total flow, F, for the sampling period in m³ at 0°C and 1 atm:

$$F = f \times t$$

Where:

- F = Total flow (m³ at 0°C and 1 atm)
- f = Flow rate (m³/h at 0°C and 1 atm)
- 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 (m³/h at 0°C and 1 atm)
- V = Roof monitor average gas velocity (m/s)
- S = Roof monitor cross-sectional area (m²)
- T = Average rooftop temperature (°C)
- P = Rooftop pressure (mm Hg)

- 273 = Addition factor converting °C to °K
- 3600 = Factor converting hours to seconds (3600 s/hr)
- 760 = Atmospheric pressure (mm Hg)

Step 2: Calculate total kg CF₄ for sampling period captured by the exhaust duct and the kg CF₄ per anode effect minute for the sampling period.

- **Step 2a.** Calculate the total kg CF₄ for sampling period captured by the exhaust duct.

$$\begin{aligned} \text{Total kg CF}_4 \text{ captured by duct for the sampling period (kg CF}_{4 \text{ duct}}) = \\ C (\mu\text{l CF}_4/\text{l air}) \times (1 \text{ l CF}_4/10^6 \mu\text{l CF}_4) \times (1 \text{ mole CF}_4/22.4 \text{ l CF}_4) \times 0.0880 \\ (\text{kg CF}_4/\text{mole CF}_4) \times 1000 (\text{l air}/\text{m}^3 \text{ air } (0^\circ\text{C}, 1\text{atm})) \times F (\text{m}^3 \text{ air @ } 0^\circ\text{C}, \\ 1\text{atm}) \end{aligned}$$

Where:

$$C = \text{Time average CF}_4 \text{ concentration } (\mu\text{l CF}_4/\text{l air}) = \text{ppmv CF}_4$$

- **Step 2b.** Calculate the total kg CF₄ per anode effect minute captured by the duct for the sampling period by dividing the total kg CF₄ from step 2a by the total anode effect minutes recorded for the test section during the sampling period.

$$\text{kg CF}_{4 \text{ duct}}/\text{AE minute} = \text{kg CF}_{4 \text{ duct}}/\sum(\text{duration of all anode effects in sample period})(\text{min})$$

Step 3: Calculate total kg C₂F₆ for the sampling period captured by duct.

$$\begin{aligned} \text{Total kg C}_2\text{F}_6 \text{ captured by duct for the sampling period (kg C}_2\text{F}_6 \text{ duct}) = \\ C (\mu\text{l C}_2\text{F}_6/\text{l air}) \times (1 \text{ l C}_2\text{F}_6/10^6 \mu\text{l C}_2\text{F}_6) \times (1 \text{ mole C}_2\text{F}_6/22.4 \text{ l C}_2\text{F}_6) \times \\ 0.138 (\text{kg C}_2\text{F}_6/\text{mole C}_2\text{F}_6) \times 1000 (\text{l air}/\text{m}^3 \text{ air } (0^\circ\text{C}, 1\text{atm})) \times F (\text{m}^3 \text{ air @ } \\ 0^\circ\text{C}, 1\text{atm}) \end{aligned}$$

Step 4: Calculate the weight ratio of C₂F₆ to CF₄:

$$\text{Ratio}_{\text{C}_2\text{F}_6/\text{CF}_4} = \text{kg C}_2\text{F}_6 \text{ duct} / \text{kg CF}_4 \text{ duct}$$

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

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

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 CF₄ and C₂F₆ as a fraction of total PFC emissions as follows:

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

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

- **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 CF₄ concentration measured by the FTIR process rather than the average concentration calculated in Step 6b.1

- **Step 6b.1.** First calculate the average CF₄ concentration from the rooftop bag or sorbent column samples for each sampling period

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

- **Step 6b.2.** Next, similar to the method in **Step 2** above, convert the average bag CF₄ concentration into kg CF₄ 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.

$$\begin{aligned} & \text{Total kg CF}_4 \text{ emitted as fugitive emissions for the sampling period} = \\ & kg_{CF_4-fugitive} = C_{CF_4-avg} (\mu l\ CF_4/l\ air) \times (1l\ CF_4/10^6\ \mu l\ CF_4) \times (1\ mole\ CF_4/22.4 \\ & l\ CF_4) \times 0.0880 (kg\ CF_4/mole\ CF_4) \times 1000 (l\ air/m^3\ air\ (0^\circ C, 1atm)) \times F (m^3 \\ & air\ @\ 0^\circ C, 1atm) \end{aligned}$$

Where:

F = total flow through potroom rooftop for sampling period (m³ air at 0°C and 1atm)

- **Step 6b.3.** Next, calculate the fugitive kg CF₄ per anode effect minute by dividing the total kg CF₄ emitted as fugitive emissions from **Step 6b.2** by the total anode effect minutes for the entire potroom for the sampling period.

$(\text{kg CF}_4/\text{AE minute})_{\text{fugitive}} = \text{Total kg CF}_4 \text{ emitted as fugitive emissions for the sampling period calculated from Step 6a or Step 6b.2 divided by the total anode effect minutes for the potroom for the fugitive sampling period.}$

- **Step 6b.4.** Calculate the fraction of total PFC emissions emitted as fugitives, $\text{Fraction}_{\text{fugitive}}$, by dividing the $(\text{kg CF}_4/\text{AE minute})_{\text{fugitive}}$ from **Step 6b.3** by the sum of $(\text{kg CF}_4/\text{AE minute})_{\text{duct}}$ from **Step 2b** and the $(\text{kg CF}_4/\text{AE minute})_{\text{fugitive}}$ as follows.

$$\text{Fraction}_{\text{fugitive}} = (\text{kg CF}_4/\text{AE minute})_{\text{fugitive}} / [(\text{kg CF}_4/\text{AE minute})_{\text{fugitive}} + (\text{kg CF}_4/\text{AE minute})_{\text{duct}}]$$

Step 7: Calculate the emission rates in $\text{kg CF}_4/\text{metric ton Al}$ and $\text{kg C}_2\text{F}_6/\text{metric ton Al}$ 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, $\text{Fraction}_{\text{fugitive}}$, as follows. The $\text{Fraction}_{\text{fugitive}}$ 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,

$$\text{Total kg CF}_4 = \text{kg CF}_{4\text{duct}} / (1 - \text{Fraction}_{\text{fugitive}})$$

Where:

$\text{kg CF}_{4\text{duct}} = \text{kg CF}_4$ obtained in **Step 2a**.

$\text{Fraction}_{\text{fugitive}} = \text{Fugitive fraction from Step 6b.4.}$, 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.

$$R_{\text{CF}_4} = (\text{Total kg CF}_4 \text{ for the sampling period}) / p \text{ metric ton Al}$$

Where:

$R_{\text{CF}_4} = \text{Aluminum specific CF}_4$ emission rate ($\text{kg CF}_4/\text{metric ton Al}$)

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

$p = \text{Metric tons primary aluminum production (from Step 5) (metric ton Al)}$

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

$$R_{\text{C}_2\text{F}_6} = R_{\text{CF}_4} \times \text{Ratio}_{\text{C}_2\text{F}_6/\text{CF}_4}$$

Where:

$R_{\text{C}_2\text{F}_6} = \text{C}_2\text{F}_6$ emission rate ($\text{kg C}_2\text{F}_6/\text{metric ton Al}$)

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

Ratio C_2F_6/CF_4 = Weight ratio of emissions of C₂F₆ to CF₄ from Step 4 (decimal fraction)

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

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

Where:

R_{CF_4} = CF₄ emission rate from Step 7b (kg CF₄/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 CF₄ is measured in the duct divided by the calculated cell days in the test section for the same period.

Step 9: If applicable, calculate CF₄ overvoltage coefficient. The overvoltage factor is expressed as kg CF₄-%CE / metric ton Al / millivolts.

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

Where:

CE = Current efficiency for aluminum production (percent)

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

7.2 **Option B: Calculating Emission Factors Based on At Line Instruments Continuously Measuring Duct PFC Concentrations**

This section presents the calculations for specific emissions of CF₄ and C₂F₆, as well as for the facility-specific slope and overvoltage parameters, when direct at line measurements of PFCs are made. The workbook included in Appendix A, Part B, provides a template for these calculations.

Step 1: For each time increment for which the instrument reports PFC concentrations calculate the kg CF₄ and C₂F₆.

$$\begin{aligned} \text{Total kg } CF_4 \text{ for the instrument measurement increment} = \\ C (\mu l \text{ } CF_4/l \text{ air}) \times (1 \text{ l } CF_4/10^6 \mu l \text{ } CF_4) \times (1 \text{ mole } CF_4/22.4 \text{ l } CF_4) \times 0.0880 \\ (\text{kg } CF_4/\text{mole } CF_4) \times 1000 (\text{l air}/\text{m}^3 \text{ air } (0^\circ\text{C}, 1\text{atm})) \times F (\text{m}^3 \text{ air } @ 0^\circ\text{C}, \\ 1\text{atm}) \end{aligned}$$

$$\text{Total kg } C_2F_6 \text{ for the instrument measurement increment} =$$

$$C (\mu l C_2F_6/l \text{ air}) \times (1l C_2F_6/10^6 \mu l C_2F_6) \times (1 \text{ mole } C_2F_6/22.4l C_2F_6) \times 0.138 \\ (kg C_2F_6/\text{mole } C_2F_6) \times 1000 (l \text{ air}/m^3 \text{ air } (0^\circ C, 1 \text{ atm})) \times F (m^3 \text{ air } @ 0^\circ C, \\ 1 \text{ atm})$$

Where:

F = Air flow for each time increment (m^3 at $0^\circ C$ 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 period²⁷.

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

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

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

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

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 Section 7.1, 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 Section 7.1, Steps 4 through 9.

8.0 QA/QC

QA/QC should be conducted in four key areas: 1) measurement system; 2) data; 3) standards; and 4) uncertainty. This section presents general guidelines for each of these areas.

Measurement System Checks. Three types of measurement system checks should be conducted: 1) leak checks; 2) recovery tests; and 3) instrument calibration.

²⁷ It is also useful to sum the emissions of CF_4 and C_2F_6 for each anode effect where the signal trace does not overlap with another anode effect. These results can be plotted versus the anode effect duration for a quality control check and to look for outlier data.

- 1) **Leak checks.** Sampling systems for all locations should be leak checked. Leaks in transfer systems at pressures under ambient pressure can be detected by closing the system and checking to see if there is a noticeable change in system pressure.
- 2) **Recovery tests.** Recovery tests check the integrity of the sampling system and instrument function by injecting a known amount of analyte and testing for the complete recovery of the injected amounts of PFC or tracer compound.
 - **Sampling system:** Recovery of sample through the sampling transfer line should be checked by rapidly exhausting a gasbag filled with a known amounts of PFCs into the sample line through the T-connection at the duct end. The resulting peak should be integrated to give the total amount of PFCs recovered. Recovery should be within ten percent of the amount released.
 - **Overall system recovery:** The accuracy of the overall analytical system should be tested by releasing approximately 200 g of CF₄ and 20 g C₂F₆ at a point far enough upstream of the sampling point to give complete mixing. Recovery should be within ten percent of the amount released. Alternatively controlled releases of a surrogate such as SF₆ or R134a may be used to test system recovery.
- 3) **Instrument calibration.** At-line instruments should be calibrated in the laboratory prior to field deployment using vendor calibration procedures. The instruments should be calibrated on CF₄ and C₂F₆ gas standards traceable to, or certified by, the National Institute of Standards Technology (NIST). In the field, the instrument response should be tested at the measurement site on appropriate standards covering the range of expected PFC concentrations calibrated before and after each 24-hour monitoring period.

Data checks. Results should be checked against expected ranges in Appendix C. If outside the range is indicated, a check of appropriate calculations and procedures should be carried out before reporting results.

Standards. Gas standards obtained from commercial sources should be measured against standards certified by NIST or a standard that is traceable to NIST.

Uncertainty. Statistical quantitative approaches should be applied to estimate uncertainty ranges for calculated Tier 3 coefficients. One approach is to use 2006 IPCC Guidelines for National Greenhouse Gas Inventories²⁸, where the overall uncertainty in the Tier 3 coefficients can be calculated as the square root of the sum of all sources of variance (U^2) in the measurement process:

$$U^2_{\text{Total}} = U^2_1 + U^2_2 + \dots + U^2_n$$

Where,

U_{Total} = percentage uncertainty in the product of the quantities;

U_i = percentage uncertainties associated with each of the quantities (aluminum production, instrument measurement, duct flow rate, etc.).

²⁸ IPCC, 2006 *IPCC Guidelines for National Greenhouse Gas Inventories*, Intergovernmental Panel on Climate Change, National Greenhouse Gas Inventories Programme, Volume 1, 2006.

9.0 Safety

Safety of location staff and measurement staff should be the highest priority. Individuals participating in measurements are responsible for acquainting themselves with the hazards that exist in the potroom environment and taking all steps to avoid injury. Before any work is initiated on site, contact should be made with the responsible location safety staff for a briefing on all local safety requirements.

9.1 Personal Protective Equipment (PPE) Requirements

While working in potroom areas location rules for personal protective equipment should be followed. Typical minimum requirements for measurement staff in potroom areas include:

- Head Protection (Hard Hat) ANSI Z89.1;²⁹
- Foot Protection (Potroom Boots) ANSI Z4.1;
- Eye Protection (Safety Glasses with nonconductive side, shields, and frames) ANSI Z87.1;
- Flame Retardant Clothing;
- Conductive apparel including rings, metal rimmed glasses, metal watch bands and metal dangling jewelry prohibited: OSHA 29 CFR 1910.333 (c) (8) Conductive Apparel; and
- Hearing protection in designated areas.

9.2 Hazards

The potroom environment has a number of key potential hazards including:

- Electrical shock hazard;
- Thermal burns;
- Moving equipment including overhead cranes as well as vehicles;
- Some processes within the smelter may release hazardous gases or fumes that would require appropriate respiratory protection;
- Uneven surfaces on which to walk;
- Falling objects; and
- Falls.

These hazards and prevention measures should be reviewed with appropriate facility personnel.

10.0 Measurement Frequency and New Measurements

Repeat measurements of CF_4 and C_2F_6 should be triggered by any one or more of the following events:

- Thirty-six months have passed since the last measurements (i.e. triennial measurements are recommended);
- A change occurs in the control algorithm that affects the mix of types of anode effects or the nature of the anode effect termination routine;

²⁹ American National Standards Information (ANSI) Z89 standard for industrial head protection.

- Changes occur in the distribution of duration of anode effects (e.g. when the percentage of manual kills changes or if, over time, the number of anode effects decreases and results in a fewer number of longer anode effects) or, for Rio Tinto Alcan control technology, when the algorithm for bridge movements and anode effect overvoltage accounting changes;

The results of measurements should be carefully documented. Results should only be used to calculate Tier 3 emission factors if the measurements were carried out using the good practices described above.

Appendix A: Data Collection, Calculations, and Reporting Template

A.1 Reporting of Results

Following the completion of the measurements, a full report should be prepared containing the pertinent details describing the facility, the sampling strategy, the measurement instrumentation and the results, including the documenting of sources of uncertainty and estimates of the magnitude of uncertainty in the calculated slope or overvoltage parameter. Data tables should contain sufficient information to allow independent checking of all reported results. Any deviations from the procedures contained in this protocol should also be reported along with the numerical results. The following parameters should be reported for each sampling period and the running time weighted average of the parameter:

- 1) CF_4 slope or Overvoltage factor;
- 2) C_2F_6 to CF_4 weight fraction; and
- 3) Total kg CF_4 and C_2F_6 per metric ton Al
 - kg CF_4 per anode effect minute collected in fume collection ducts
 - kg CF_4 anode effect minute emitted as fugitives where fugitive emissions are measured.

The following data collection templates are for the 1) time average bag or sorbent column sampling, and 2) near real time measurement approaches:

a. Time Average Sampling

A data collection form is included in the Excel workbook at the location below for time average bag sampling that includes forms for both duct sampling and for potroom rooftop monitor sampling.



"PFC Bag Sampling
Data Workbook_rev8

b. Near Real Time Measurements

A data collection form is included in the Excel workbook at the location below for near real time measurements.



Microsoft Excel
Worksheet

Appendix B: Suppliers

The following list of suppliers is not intended to be a comprehensive list of all suppliers of the equipment. Rather, this list was compiled from readily available information supplied by the authors and reviewers.

1. Process mass spectrometers, ABB, www.abb.com, Process Instruments
2. Multi-layer sample bags, <http://www.calibrated.com/home.htm>
3. Photoacoustic infrared filter photometer, www.innova.dk
4. FTIR spectrometers:
 - a) Midac, www.midac.com
 - b) Gasmeter, www.gasmet.fi
 - c) MKS, www.MKSinst.com
 - d) IMACC, www.imacc-instruments.com
5. Sample pumps:
 - a. Gast Manufacturing, www.gastmfg.com
 - b. KNF Neuberger, <http://www.knf.com/usa.htm>
6. Low volume sample pumps:
 - a) A.P. Buck, Inc., www.apbuck.com
 - b) SKC Inc., <http://www.skcinc.com/skc.html>
7. PFA Teflon sample tubing:
 - a) Omega Engineering, www.omega.com/tubing/flexible tubing/teflonpfa.html
 - b) Swagelok, www.swagelok.com/
8. Gas standards:
 - a) Matheson Tri-Gas, www.matheson-trigas.com/
 - b) Scott Specialty Gases, www.scottgas.com

Appendix C: Expected Range of Results by Technology

The following range of slope values and overvoltage coefficients are taken from analysis of reported prior measurement data and are calculated to include approximately 95 percent of the expected distribution of values.

Table C: Range of Slope Values

	CF₄ slope (kg CF ₄ /t Al)/(AE min/cell-day)	C₂F₆ Weight Fraction ³⁰ (kg C ₂ F ₆ /kg CF ₄)
CWPB or PFPB	0.07 – 0.21	0.03 – 0.24
SWPB	0.20 - 0.35	0.14 – 0.36
VSS	0.04 - 0.18	0.02 – 0.084
HSS	0.02 – 0.15	0.02 – 0.84

	CF₄ overvoltage coefficient (kg CF ₄ t Al/ millivolts/cell-day)	C₂F₆ Weight Fraction (kg C ₂ F ₆ /kg CF ₄)
PFPB	0.60 – 2.3	0.03 – 0.24
SWPB	2.4 – 4.9	0.14 – 0.36

Source: J. Marks, selected measurement results from data reported in the literature and private communications.

³⁰ The C₂F₆/CF₄ weight fraction parameter is the same for both slope and overvoltage methodology.

Appendix D: Checklist

Check Item	✓	Bookmark
<i>Contact Smelter Staff</i>		
• Obtain site overview		
• Obtain safety orientation		
• Assess safety requirements		Safety
– Personal protective equipment requirements		
– Site hazards		
• Obtain historical data to establish expected ranges of PFCs in measurements		
• Assess if smelter is operating in a state of normal process control		
– Current anode effect frequency and duration performance similar to prior months		
– No power interruptions		
<i>Obtain Process Data</i>		Process data needs
• Type of reduction technologies		
• Bath chemistry		
• Definition of anode effects		
• Overvoltage data		
• Production data		
– Tap weights		
– Line current and current efficiency		
– Net anode consumption and anode impurities assessment		
• Computer control system scan rate and anode effect kill routine		
<i>Select Sampling Sites</i>		Sampling locations
• Establish separate sampling site for each operating cell type		Cell technology
• Check if more than one type of anode effect control algorithm is used for controlling anode effect termination in different potlines		Control algorithm
• Assess whether fugitive emissions are expected to be greater than 10 percent of total emissions. Make decision on measuring fugitives or calculating fugitives based on capability of measurement methodology.		Fugitives
• Select representative site for background sample collection		Background sampling
• Conduct duct flow homogeneity tests, if required.		homogeneity
• Select duct locations		

Check Item (continued)	✓	Bookmark
<ul style="list-style-type: none"> • Make choice on continuous measurement or average sampling and measurement method based on availability of instrumentation and experience of measurement staff: 		Average Concentration Field instruments Lab based instruments
<i>Select instruments for laboratory based measurement methods</i>		
<ul style="list-style-type: none"> • GC/MS 		
<ul style="list-style-type: none"> • FTIR 		
<i>Select instruments for field measurement methods</i>		
<ul style="list-style-type: none"> • Mass spectrometer 		
<ul style="list-style-type: none"> • TDLAS 		
<ul style="list-style-type: none"> • PAS 		
<ul style="list-style-type: none"> • FTIR 		
<i>Commission equipment at site</i>		
<i>Conduct QA/QC tests at site</i>		
<ul style="list-style-type: none"> • Measurement system checks 		QA_QC checks 1 to 3
<ul style="list-style-type: none"> – Leak tests 		
<ul style="list-style-type: none"> – Recovery tests 		
<ul style="list-style-type: none"> • Instrument calibration 		
<ul style="list-style-type: none"> • Data checks <ul style="list-style-type: none"> ○ Check results against expected range of values in Appendix C ○ Construct a plot of CF₄ emissions versus anode effect minutes for the test periods and examine for and check any outlier data ○ Construct a plot of CF₄ emissions versus individual anode effect duration if temporal resolution of measurement methodology is capable and check of any outlier data 		
<ul style="list-style-type: none"> • Standards 		
<i>Calculate and report results</i>		
<ul style="list-style-type: none"> • Complete Excel workbook with sampling and measurement data depending on whether at line measurements were made, or, alternatively, average samples are taken. 		Average sampling work book Real time workbook
<ul style="list-style-type: none"> • Check that calculated Tier 3 coefficients from measurements are acceptable 		Sampling time Data checks
<ul style="list-style-type: none"> • Document results along with an estimate of uncertainty and notation of any deviations from the protocol's recommended practices. 		Reporting Uncertainty

Appendix E: References and Information Sources

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