

# Light Metals 2014

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## Comparing Different Measurement Approaches to Characterize All PFC Emissions

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### Abstract

Different measurement approaches have been used to characterize PFC emissions coming from aluminum smelting. In the past, those techniques were developed mainly to measure PFC emissions during the so called Anode Effect (AE). More recently, the variable but notable presence of PFC emissions outside AE was confirmed by many authors. In this paper, we analysed the results obtained by using two different PFC measurement approaches: one using an FTIR with in-situ and real time analysis, and one using an extractive procedure with sampling bags and GC-MS analysis integrating all emissions over an extended period of time. Results for the same sampling location are given for both methodologies and their pros and cons are discussed in light of a proper accounting of non-AE PFC's. These will need to be carefully considered in future measurement campaigns to provide the most accurate information depending on user needs.

### Introduction

Since the beginning of the measurement of perfluorocarbon (PFC, mainly  $CF_4$  and  $C_2F_6$ ) emissions coming from the aluminum industry, many different measurement techniques have been used. Among the more cited in the published studies, there are the photoacoustic spectrometer [1]; Tunable Diode Laser [2, 3], the Fourier Transform Infrared (FTIR) [4, 5, 6] and the sorbent materiel (bag, tube) sampling coupled with gas chromatography with mass spectrometric detection (bag/GC-MS) [7, 8, 9]. The main differences between the latter and the first three techniques are that: 1. it requires less equipment in-situ, as the analysis is done in a laboratory, 2. it ensures the inclusion and characterization of all emissions, and 3. it offers limited possibilities to evaluate short-time dynamic and interaction between PFC emissions and operation parameters. Since 2005, the Arvida Research and Development Center (ARDC) has mainly used the bag/GC-MS technique when characterizing PFC emissions from Canadian smelters.

All those measurement techniques were considered to yield comparable results when characterizing PFC emissions, as can be found in the last version of the official *US EPA Protocol* [11]. Until then, PFC emissions were believed to occur almost exclusively during the Anode Effect event (AE). However, in the last few years, we have seen a number of publications highlighting the presence of non-AE PFC emissions [4, 5, 6, 10], and the occurrence of other forms of greenhouse gases ( $C_3F_8$ ;  $CClF_3$ ) [9]. In light of those new developments, it became important for Rio Tinto Alcan to analyze the possible differences between the bag/GC-MS methodology against a continuous measuring equipment, to ensure comparability of reported results or transition between one method and another at one particular

site. With the recent implementation of carbon regulation around the world, the comparability of the PFC measurement campaign is becoming an important economic as well as environmental issue for the industry.

### Materials and Methodology

In order to do this comparison, a PFC emissions measurement campaign was performed by J. Marks & Associates and the ARDC, on Point Feed Prebake cells at the Alma smelter located in Québec, Canada. This smelter uses the RTA AP35 pot technology. The analyses took place from 22 April to 3 May 2013.  $CF_4$  measurements were made with a Temet Model DX4000 FTIR spectrometer operating with a spectral resolution of  $7.8\text{ cm}^{-1}$  with 10 scans per second, with results averaged over a 20-second time period. A continuous sample was pumped to the instrument via Teflon® transfer tubing. The transfer line was equipped with a moisture trap (Drierite desiccant material) in order to remove most of the water in the sampled gas prior to being introduced into the FTIR. The sampling flow rate was set at 2 L/minutes. Tedlar® bag samples were used to collect a fraction of the gas downstream from the exit of the FTIR spectrometer, with a peristaltic pump at a flow rate set to 0.006 L/minutes. Figure 1 below shows the sampling set-up. The samples collected in the bags were analyzed at the Rio Tinto Alcan ARDC laboratory using a GC-MS..

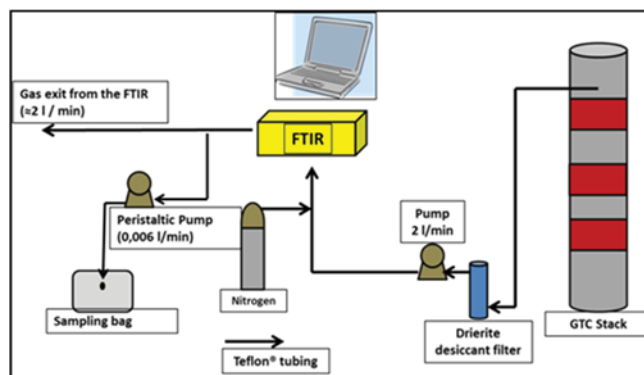


Figure 1. PFC Sampling set-up at the Gas Treatment Center (GTC) for the comparison of the FTIR and the bag/GC-MS method.

Sampling was made at two locations: one was made from a port on the Gas Treatment Center (GTC) exhaust chimney, to sample the sector served by this GTC. The other sampling location was straight at the exhaust of a specific cell, equipped with continuous anode current distribution reading at each anode (1second data), to better understand the relation between  $CF_4$  dynamic and cell

parameter. For the single cell measurement, a small alumina filter was added to the system to remove HF prior to the FTIR. The small amounts of fugitive PFC emissions escaping collection in the duct system through the roof top were calculated based on the estimated fume collection fraction for the lines. The measurements were carried out according to the *US EPA Protocol* [11]. The results obtained with the two measurement methods will be presented and discussed, by looking solely at the CF<sub>4</sub> emissions.

## Results and Discussion

### Comparison of Measured CF<sub>4</sub> Concentrations

Table 1 shows the results of CF<sub>4</sub> concentrations obtained by FTIR and the bag/GC-MS methods. The reported FTIR values refer to the average concentration measured over the same period when the bag sample was collected. Unfortunately, two bag samples were lost during the first two days, leaving four bags with different sampling times for the comparison at the GTC. The differences observed at the GTC range from 10 to 30% and from 11 to 60% at the cell. The high % variations observed at the cell contrast with the low variation in terms of ppbv, showing that most of the time, the concentrations measured were close to the detection limit, calculated to be around 10 ppbv for the FTIR, and below 1 ppbv for the bags/GC-MS. Two AE were recorded during the cell measurement: a short one for the first sample and a long one for the seventh sample. For the latter, the value reported by the FTIR was extrapolated over the linearity range. Therefore, this sample was discarded and not used in the data processing.

Table 1: Sampling results for CF<sub>4</sub> concentrations using both methods

Location	Sample #	Sample time (hours)	Bag/ GC-MS measured CF4 (ppbv)	FTIR CF4 measured (ppbv)	Difference (%)	Difference (ppbv)
GTC	1	3,85	454	502	-10%	48
GTC	2	19,80	145	120	22%	-26
GTC	3	24,00	63	78	-20%	15
GTC	4	75,70	49	69	-30%	21
Cell	1	23,83	199	180	11%	-19
Cell	2	1,00	20	26	-26%	7
Cell	3	1,00	8	15	-46%	7
Cell	4	1,00	4	11	-60%	7
Cell	5	1,00	0	<LDL	NA	NA
Cell	6	23,79	18	31	-43%	14
Cell	7	1,00	5 843	> LL	NA	NA
Cell	8	0,50	14	26	-47%	12

Albeit the observed variation in %, when averaging the results for the whole sampling period (Table 2), the differences fall to 8% at the GTC, and at 14% if the measured concentrations are weighted with the time of the sample time. For the cell measurement, the difference falls to 9%, or to only 2%, when the concentrations are weighted with the sample time.

The relatively high variation between each sampling may be subject to some discussion. One possible explanation is that the gas flow rate pumped from the GTC stack through the FTIR was not constant throughout all the collection periods, varying between 2.0 – 2.5 liters per minute.

Table 2: Averaged comparison results for CF<sub>4</sub> concentration using both methods within their calibration zone

Comparison bag/GC-MS vs FTIR		CF4 ppbv	FTIR CF4 ppbv	Difference (%)	Difference (ppbv)
GTC	Sample Average	178	192	-8%	15
GTC	Ponderate with sampling time	80	93	-14%	13
Cell	Average without AE	38	41	-9%	5
Cell	Ponderate with sample time without AE	100	98	2%	2

It is not critical for the correction of CF<sub>4</sub> emissions with the FTIR, since lower flows spread the CF<sub>4</sub> signal over longer periods of time with lower peaks, while higher flows give higher peaks for shorter times. However, it may have had an impact on the bag samples, which were pumped from downstream of the FTIR exit at a very steady rate with the peristaltic pump. Therefore, periods of lower flows from the stack to the FTIR will be weighted higher in the bag samples. This source of variation should, nonetheless, tend to equilibrate during a representative sampling. As a matter of fact, it is very interesting to note that within their calibration zone, the averaged results comparison showed differences inferior to the IPCC reported uncertainty of ±15% for site specific PFC measurement [12]. This fact tends to show that both methods are in fact comparable, but observed variation tends to support the need to take shorter and more numerous samples with the bags/GC-MS method.

### Measured CF<sub>4</sub> Emission Rate

With the FTIR, it was possible to measure the CF<sub>4</sub> emission rate per second of AE (Figure 2). The impact of AE duration is extremely important, with an emission rate 10 times higher for AE less than 5 seconds versus an AE of 60 seconds or more.

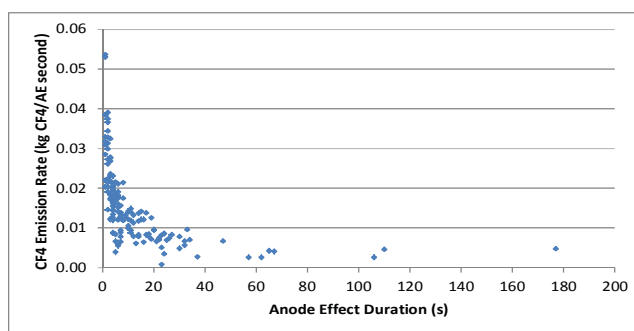


Figure 2: CF<sub>4</sub> emissions' rate per second of AE, for each sampled AE below 200 seconds.

A somewhat similar relation was observed within the bag sample (Figure 3), but with much less resolution, as only four samples were analyzed, in which we could only compare the average AE duration per sample. Having those results only, it is impossible to appreciate the very high emission intensity during the first seconds of the AE, which is reflected in the difference between the ordinate scales of each figure. Moreover, the sample integrates non-AE PFC background level, possibly interfering with the impact of average AE duration on the overall measured emission rate. Clearly, the FTIR allows for a more accurate comprehension of the single AE dynamic.

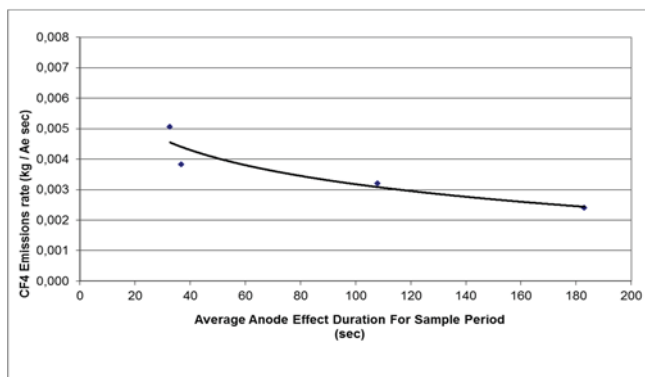


Figure 3: CF<sub>4</sub> emissions' rate per average AE second per bag sample.

#### Measured CF<sub>4</sub> Slope Factor and Impact of Non-AE PFC Emission

With the FTIR, more than 330 AE were sampled. The average CF<sub>4</sub> IPCC Tier 3 Slope Factor calculated for the sampling period is 0.089 (kg CF<sub>4</sub>-/T Al)/(AE min/cell day) when calculated from the sum of CF<sub>4</sub> emissions from anode effects and emissions not associated with anode effects. The Slope Factor, considering only CF<sub>4</sub> emissions from AE, is 0.078. This Slope Factor is lower than the IPCC Tier 2 default Slope Factor of 0.141 [12, 13], but is within the 95% confidence limit expected from the variance of the data from which the Tier 2 default Slope factor was calculated. During this sampling, the non-AE PFC emissions represented 12% of the observed PFC emissions, at between 10-15 ppbv in average. This level of difference is below the IPCC reported uncertainty for PFC emissions measurement. It is also below the measured CF<sub>4</sub> concentration difference observed between the bag/GC-MS and the FTIR for this campaign, at the GTC.

Those results represented a significant drop compared to the previous results obtained during the last PFC measurement campaign in 2008. The last slope factor measurement at the facility, with the bag/GC-MS method, was more than 200% higher, at the other end of the expected results range from the IPCC. A difference in AE distribution in function of their duration cannot explain this change as the proportion of short AE was much higher in 2013, with around two-thirds of recorded AE below 10 sec, compared to 16% in 2008. As there was no change in the AE definition in the cell control system, our main hypothesis to explain this situation is that the relative level of non-AE-PFC emissions was much higher in 2008. First, we know that the AEF per cell was significantly lower in the 2008 sampling campaign, increasing therefore the relative weight of non-AE PFCs. We also know that the bag samples integrate non-AE PFC, which has been documented to be in some cases, quite significant in terms of their relative contribution to the overall PFC emissions [4]. A two-fold higher non-AE PFC emission in 2008 combined with the lower total AED would explain the change in the slope factor. It is impossible to verify this hypothesis, as no specific characterization was made for non-AE PFC emissions in 2008. It is clear, however, that a higher level of non-AE PFC emissions coupled with very low recorded total AED can have a significant impact on the slope factor calculation, if both are not being distinguished. It can be relatively easy to calculate the non-AE PFC contribution with a continuous monitoring approach such as

the FTIR, provided it is well calibrated and that its detection limit is low enough. When using the bag/GC-MS approach, the characterization of the PFC from or outside AE is more fastidious. It requires a good understanding of the non-AE PFC emissions occurrence, to elaborate a sampling procedure generating enough bags that are representative of all the production cycle, without recorded AEs. To this day, all sampling using the bag/GC-MS method within Rio Tinto Alcan smelter included the non-AE PFC emissions when calculating the slope or overvoltage factor.

More generally, this raises the question of the representativeness of the approach consisting in calculating PFC emissions through a factor solely based on total AE duration (or overvoltage) when this duration (or overvoltage) drops down close to zero in the most advanced smelters. The current model predicts zero PFC emissions when recorded anode effects are eliminated; however, emissions may still be measured due to localized anode effects that are not propagated to the entire cell and do not result in average cell voltage exceeding the anode effect trigger voltage.

#### Understanding the Impact of Pot Condition or Operation on Non-AE PFC Emissions

To better understand the dynamic of non-AE PFC emissions and evaluate the impact of pot condition or day-to-day operation on the PFC emission, the FTIR was coupled with the individual anode current distribution reading. The continuous measurement of PFC with the FTIR during two days of sampling is shown in Figure 5. Interestingly, it was possible to link most of the non-AE PFC emissions recorded during this sampling with specific operation or pot condition. As previously highlighted in the literature, significant level of PFC emissions was recorded during anode change [5, 6, 10] and metal tapping [10]. Moreover, it was observed that PFC emissions could be released before the AE start, when pot instability could be measured or when a stopped feeder was perturbing alumina feeding [6, 14].

When the continuous PFC emission is coupled with the anode current reading, it is possible to appreciate the dynamic leading to the non-AE PFC, as described in recent studies [14, 15, 16]. In multiple-anode-cells, specific event or condition can lead to a raise in the current uptake of one or more of the anodes, increasing their anode current density until the alumina concentration at the anode surface approaches zero. Thereafter, the current abruptly drops back to a much lower value, and PFC is being evolved, even when the cell is not computing AE. For example, during anode change, the current from the changed anode is redistributed, initiating this chain of events. But it could also be observed in our study that anodes near the tapping end tend to pick up less current while anodes near the opposite end tend to pick up more current (Figures 6 A and B), probably also initiating the chain of reactions leading to non-AE PFC. In that case, no anode effect followed the metal tapping and the highest voltage value recorded during that period was 4.02 V, as the current distribution returned to its normal state after the metal tapping event. This phenomenon may be attributed to anode cathode distance being locally modified.

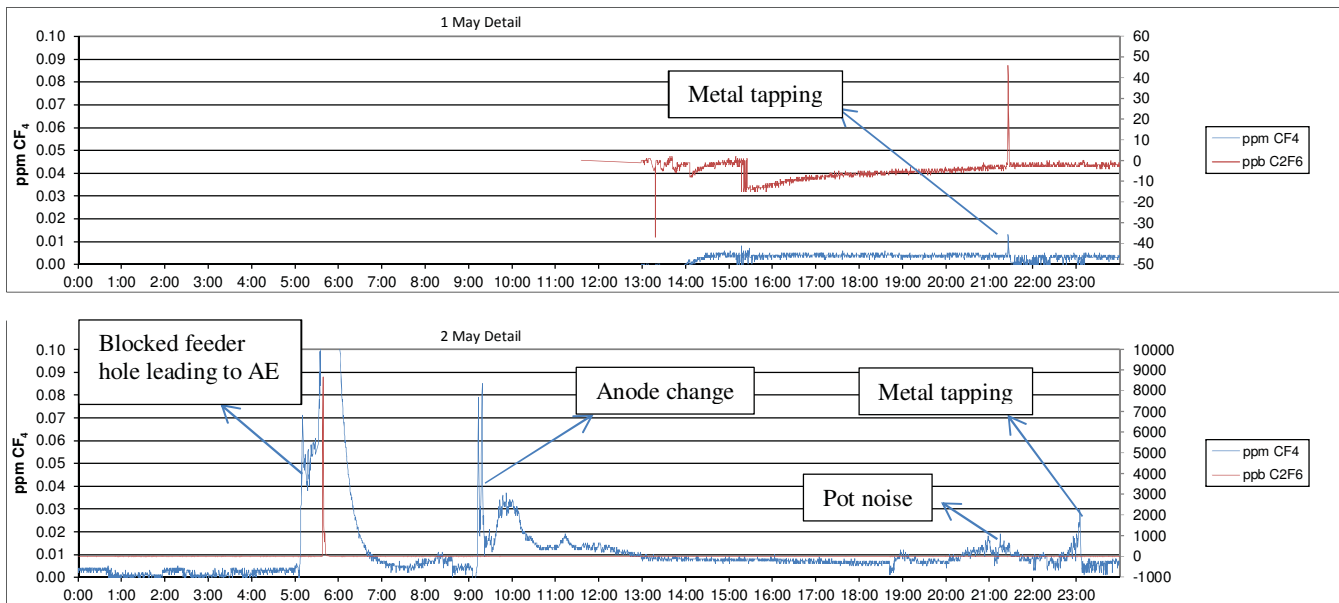


Figure 5: Dynamics of PFC emissions during the single cell measurement.

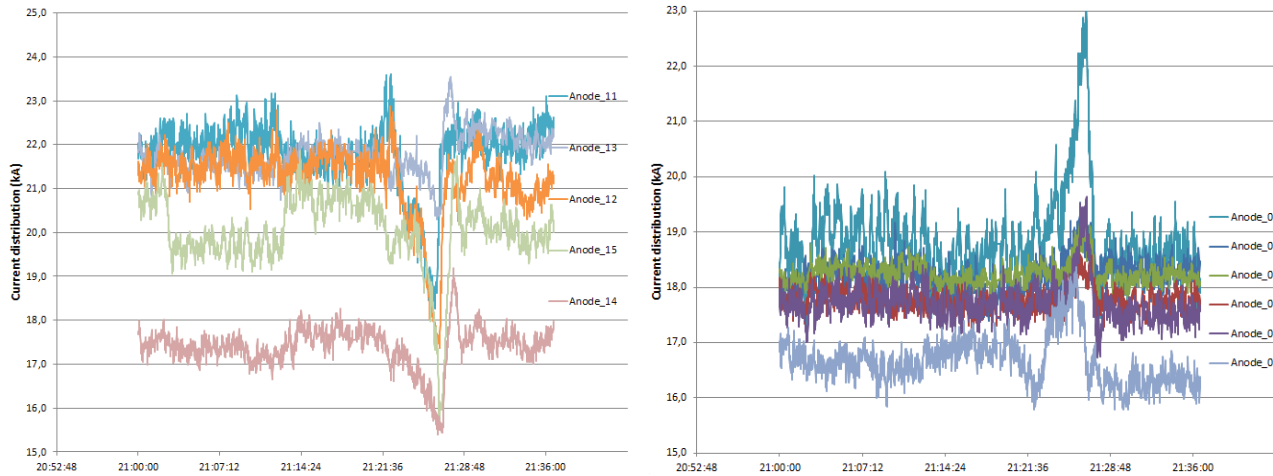


Figure 6: Current distribution for some anode of a single cell, during the metal tapping on 1<sup>st</sup> May 2013 (left side: some anodes near the tapping end; right side: some anodes near the opposite end).

On 3<sup>rd</sup> May, at around 5:30 in the morning, an event related to anode covering with a blocked feeder, caused high amperage variation on a specific anode (#12 in figure 7), which probably initiated the generation of PFC emissions. At first, anode No. 12 was picking up current at the same level as the other anodes. Thirty minutes before the anode effect, it suddenly began to pick up more current. Finally, it demonstrated a very variable behavior four minutes before the anode effect.

Clearly, more analyses are needed to understand the full relationship between certain events and the consecutive chain of reactions leading to PFC emissions. Our present research aims at better understanding the different operational procedures/conditions, such as anode change and pot instability, impacting the recorded level of non AE PFC emissions. The FTIR, coupled with anode current distribution, proves to be a very powerful tool for this. A detailed understanding of these relationships may lead to strategies for mitigation of PFC

emissions and for more efficient cell operation. On the other hand, the bag sample technique cannot give the specific dynamics of the PFC emissions and its accurate relation with pot condition, but it can give a very accurate measurement of the total PFC emitted during a certain operational event. It can easily be used to characterize all PFC emissions during a certain predictable event, such as pot start-up for example, where the timing is clearly defined. Maltais et al. did so a few years ago [17]. It can also be used to complement FTIR sampling at the cell to accurately measure the level of emissions during a powerful anode effect, which will probably be out of calibration range for a portable FTIR calibrated to measure low PFC level. Another advantage of complementing the single cell measurement with bag sample is the possibility to characterize other PFC compounds [9]. During this measurement campaign, no other PFC could be identified.



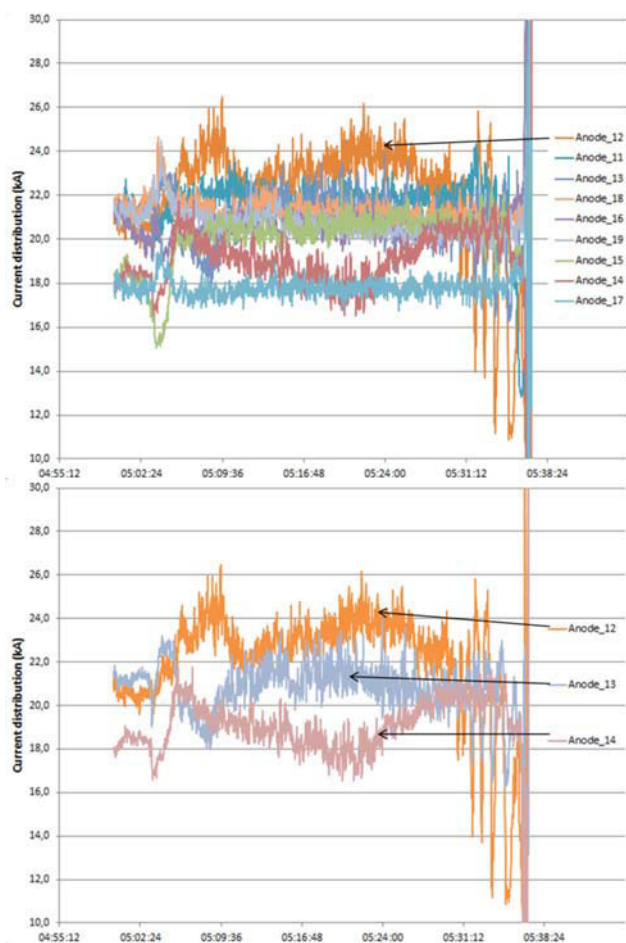


Figure 7: Pot instability leading to a specific anode behavior. The graph below focuses on specific anode behavior showing the highest variation.

### Summary and Conclusion

In summary, it can be said that the results of this study show that both analyzed methods are comparable, but that the level of information that can be gathered differs. Depending on the way you deal with the non-AE PFC emissions within each method, the reported PFC emissions following the IAI and IPCC tier 3 guidance [12,13] can be affected. The non-AE PFC emissions can more easily be separated with the FTIR equipment, while necessarily being integrated with the sample bag technique, unless many short and representative samples are taken, when no AE are being recorded, requiring complex planning. Integrating the non-AE-PFC emissions in the calculated slope factor can be representative if the operating conditions are very stable (AEF; AED; non-AE PFC emissions level), but can be exaggerated or minimized if significant change in anode effect performance occurs after the campaign. Because we still lack reliable indicators for predicting or controlling the non-AE-PFC emissions, more research is needed to fully understand their dynamics and variation. The FTIR, coupled with in-depth process analysis tool such as the continuous anode current monitoring, can provide very reliable information in that regard. In a R&D perspective, the bag/GC-MS can be used as a complement, to better characterize high AE concentration or other possible compound. In an

operational mode, this technique can be used with good accuracy and relative simplicity, to measure PFC emission from a certain event, such as a pot start-up, or the evolution of the overall PFC emissions over a certain period of time. The outcomes of our comparison also highlight the need to develop a new methodology to better integrate, or separate, the non-AE PFC emissions to improve the representativeness and the comparability in GHG reporting.

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