Alcoa Mosjøen

Measurements of CF_4 and C_2F_6 emissions from Alcoa Aluminium's smelter at Mosjøen, Norway

Norbert Schmidbauer, Ove Hermansen, Chris Lunder

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AUTHOR(S) Norbert Schmidbauer, Ove Hermansen, Chris Lunder		QUALITY CONTROLLER Kjersti K. Tørnkvist
REPORT PREPARED FOR Alcoa Mosjøen, 8663 Mosjøen		CONTRACT REF. Ellen Bromstad Myrvold

ABSTRACT

NILU performed a test campaign for measurements of CF_4 and C_2F6 for stack emissions at Alcoa Mosjøen Smelter. Time-integrated samples were taken with evacuated canisters combined with low-flow restrictors for continuous sampling periods as long as 4 weeks. The samples were analyzed at NILU with a Medusa preconcentration method combined with GC-MS SIM. As a main conclusion, time integrated sampling together with Medusa GC-MS methodology is a very precise alternative to the traditional attempts to quantify PFC-emission.

NORWEGIAN TITLE

Målinger av CF_4 og C_2F_6 utslipp fra Alcoa Aluminium Mosjøen

KEYWORDS

CF_4 and C_2F_6 emissions	Aluminium industry	GC-MS Medusa

ABSTRACT (in Norwegian)

NILU utførte en testkampanje for målinger av CF_4 og C_2F_6 fra skorsteinsemisjoner ved Alcoa Mosjøen. Tidsintegrerte prøver ble tatt ved hjelp av evakuerte stålbeholdere kombinert med gass-fløde restriksjoner over en tidsperiode på 14 dager. Prøvene ble analysert på NILU med en Medusa oppkonsentreringsenhet som er koblet til en GC-MS i SIM modus. Metoden viser seg til å være et godt alternativ til de tradisjonelle emisjonsberegninger.

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Contents

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1 Introduction

Tetrafluoromethane, CF_4, and hexafluoroethane, C_2F_6, are the two most abundant PFCs in the atmosphere and are both potent greenhouse gases with long atmospheric lifetimes, currently estimated at 50,000 and 10,000 years, and global warming potentials of 6,630 and 11,100 over a 100-year timescale. Emissions from the aluminium industries and the semiconductor industries are the main sources for the increasing atmospheric background levels of these gases.

In 2009- at Hydro Australia's smelter Kurri Kurri - CSIRO performed measurements of perfluorocarbons (PFC) with canister-sampling followed by off-line analysis with Medusa GC-MS (Fraser 2013). The Kurri Kurri study showed that this method was very cost effective and more precise than FTIR or TDL measurements and very suitable for long-time sampling.

Hydro Aluminium Norway contacted NILU in 2018 to investigate the possibilities to establish a system for precise time-integrated PFC-measurements for both stack emissions, diffusive emissions and measurements at cell outflow-ducts. Alcoa Mosjøen joined the project in 2019.

NILU has long experience with PFC-measurements and is equipped with the most sophisticated instruments for PFC-measurements – the Medusa GC-MS. NILU also has long experience with time-integrated sampling into stainless steel canisters followed by off-line Medusa GC-MS analysis.

PFC-emissions from the aluminium industry are reported to national authorities according to detailed protocols prepared and recommended by the International Aluminium Institute (IAI) in close cooperation with national authorities like the U.S. Environmental Protection Agency, as well as IPCCs three-tiered PFC inventory approach. These very detailed protocols are based on campaigns with short-duration measurements using FTIR or QCL-lasers and calculations based on relationships between logged anode effect process parameters – either anode effect minutes per cell day or overvoltage.

Estimates from global atmospheric measurements are suggesting periods of both over-accounted emissions (nearly 40 % between 1996 and 2002) and under-accounted emissions (about 40% between 2003 and 2010) (Wong 2015). Despite significant progress from the aluminium industry in understanding and reducing their emissions over the last three decades, the global model emissions for CF_4 and C_2F_6 - using atmospheric measurements as input - continue to rise and are significantly larger than those currently reported by industry and governments. There is still strong evidence for unaccounted PFC-emissions from the aluminium industry as a whole, but also quite large regional discrepancies with special focus on East Asia. Environmental legislation of PFC-emissions may in the near future move towards online-emission monitoring or time-integrated sampling methods in combination with precise off-line measurement techniques.

As the main goal of this first project, Hydro Aluminium in co-operation with Alcoa Mosjøen and NILU agreed to validate and further elucidate to what extent canister time-integrated sampling together with Medusa GC-MS methodology can be used and further improved as an alternative to the traditional attempts to quantify PFC-emission.

2 Background

2.1 Time-integrated sampling

"Time-integrated sampling or concentration representative sampling is when a sample is taken over a period of time, in which the concentration of a species is equal to the averaged concentration of an imaginary or real continuous analysis of the same species over the same time period".

Using evacuated stainless steel canisters together with a restrictor with linear flow properties will give representative air samples. PFC's are very long lived and stable compounds as well as very volatile – making them ideal to be sampled into canisters and stored without analytical drawbacks.

2.2 Measurements with Medusa GC-MS

The **A**dvanced **G**lobal **A**tmospheric **G**ases **E**xperiment (AGAGE) has been measuring the composition of global atmosphere since 1978, www.https://agage.mit.edu/

AGAGE's latest measurement upgrade is a preconcentration system called Medusa. For details like flow schemes, temperature settings, pressure regimes, adsorbent and columns (see Miller 2008). At the heart of the Medusa is a cold plate which maintains a temperature of - 175° C which cool two traps to about - 165° C. Each trap can be independently heated resistively from - 165° C to +200° C. The use of two traps with wide programmable temperatures ranges, coupled with the development of appropriate trap absorbents, permits the desired analytes from 2-liter air samples to be effectively separated from more-abundant gases that would otherwise interfere with chromatographic separation or mass spectrometric detection, such as N_2, O_2, Ar, H_2O, CO_2, CH_4, Kr and Xe. Importantly, the dual traps also permit the analytes to be purified of interfering compounds by fractional distillation and re-focusing from the larger first-stage trap (T1) onto a smaller trap (T2) (Figure 2) at very low temperatures, so that the resulting injections to the Agilent 5973 GC-MS are sharp and reproducible. A Linux operating system runs both the Medusa "front end" and the GC-MS in selective ion mode (SIM). This software includes the mass/charge ratio as a variable, as well as the many control and diagnostic parameters of the Medusa. Blanks and instrument linearities are measured routinely. An important advance in the Medusa is its ability to check its linearity by injecting a wide range of standard gas volumes. Such linearity and composition-independence are critical to accurate calibration, especially when propagating synthetic primary standards or when measuring samples spanning wide concentration ranges. The Medusa system uses a high precision integrating mass flow controller (MFC) for improved measurement of sample volumes. The Medusa systems are producing exceptional routine precisions. The practice of alternating ambient air and calibration gas analyses obtain the highest precision measurements. By using quantifier (target) and qualifier ions for each measured species, the Medusa also offers improved peak identification and reduced susceptibility to interference by co-eluting species.

Instrument calibration is performed against the standards produced at Scripps Institution of Oceanography La Jolla, California, USA (SIO) for use with the Medusas. SIO has maintained the Central Laboratory for standards of halogenated gases within AGAGE for the last 4 decades and their scale together with the scale of NOAA (National Oceanic and Atmospheric Administration) are those scales which are used for reporting global atmospheric background concentrations.

Medusa measurements of the global atmospheric background concentrations of halogenated gases are very precise – usually within less than 1 % precision - and can be used to measure concentration levels far lower than FTIR and QCL instrumentation.

3 Project milestones, progress and achieved results

3.1 Method development prior to sampling at Alcoa

Before sampling at Alcoa Mosjøen, several test sampling campaigns were carried out at Hydros aluminium plant at Husnes during 2021 and 2022 in order to gain first experience with concentration levels, sample amount, necessary dilution steps, possible interferences with co-emitting compounds like water, particles, SO2, CO2 or other halocarbons or hydrocarbons. Integrity and stability of the PFC levels in the canisters over longer time periods were investigated.
Samples were also analyzed for the whole AGAGE range of more than 40 additional halogenated compounds, C2-C9 hydrocarbons and some sulfur containing compounds (H_2S , COS and CS_2) as well as CO_2 , CO and Methane levels using a Picarro G2401 Laser Analyzer.
Samples were pressurised in the canisters prior to analysis by adding zero air. Then different amounts of sample were injected into the Medusa to check linearity of the instrument response and to enable measurement levels close to the ambient air levels in the reference standards.
Overall - the samples did not cause any problems to the Medusa-preconcentration unit. No contamination issues due to high loads of compounds – no problems with the dilution of the canisters with zero air – no interferences with the target compounds. The linearity range was wide enough that it did not pose any problem to find the right sample size for the final analysis of PFC-14 (CF_4) and PFC-116 (C_2F_6).
Observations during the experiments showed that compounds like F-11, F-12 and SF_6 (and many other halocarbons) can be used as conservative tracers – their concentrations levels were identical to the real background levels and can therefore be used as a true measure for the accuracy of the dilution steps.

3.2 First site visit

The first site visit at Alcoa Mosjøen took place April 25 and 26, 2022 when Salman Yemane hosted the visit of Ove Hermansen and Norbert Schmidbauer from NILU. During the visit suitable sampling spots were identified and necessary information for technical issues like flange diameters, chimney flow etc. The technical staff at the site was introduced to the sampling procedures.

3.3 Test of CSIRO's sampling equipment

CSIRO Australia have successfully performed similar measurements at the Kurri Kurri aluminium smelter in Hunter Valley, NSW, Australia. Part of this project was to compare their equipment with NILU's equipment to establish a similar and improved method for time integrated sampling and analysis.
For this project, NILU rented four sets of 30 litre stainless steel canisters from CSIRO together with flow restrictors (0.004"ID tube 1,2 m length) and 4 pressure loggers for the monitoring the sample flow. The linearity of all four canisters and restrictors was tested and confirmed at the laboratory – all four canisters had an inflow rate that would allow more than one month of time-integrated linear inflow. Tests and sampling were carried out in parallel with NILU's equipment.

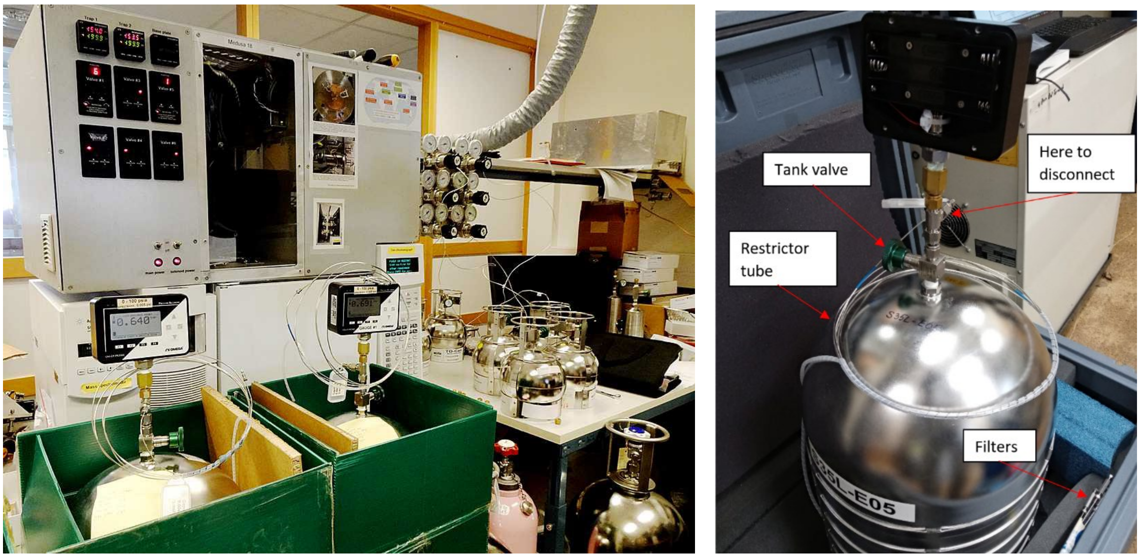

Figure 1&2: The 2 photos above showing the 30 litre canisters from CSIRO connected to the Medusa at NILU, Kjeller.

3.4 Canister cleaning

Testing the cleaning of the canisters before re-use in the next sampling campaign.

Cleaning of the canisters before and after use was done with a turbomolecular high vacuum pump at 10 $^{-5}$ mbar for 12 hours at 60 ° C – the canisters did not show any measurable levels of PFCs when refilled with Zero air.

3.5 Measurement campaign and results

The start of the measurements took place on august 29th 2022 with Asbjørn Kjønnås hosting the visit of Ove Hermansen and Norbert Schmidbauer from NILU.
Sampling started at 14:04 August 29th and ended at 12:40 September 13th.

Figure 3: The samples taken with a down facing inlet tube inside the stack in order to prevent water clogging. CSIROS four canisters with pressure logger were used during the campaign at Mosjøen. For each of the two chimneys one inlet line was split into two different flow restrictors (CSIRO's, 0.004" tubing and NILU's critical orifice) after passing a particle filter and HF-scrubber.

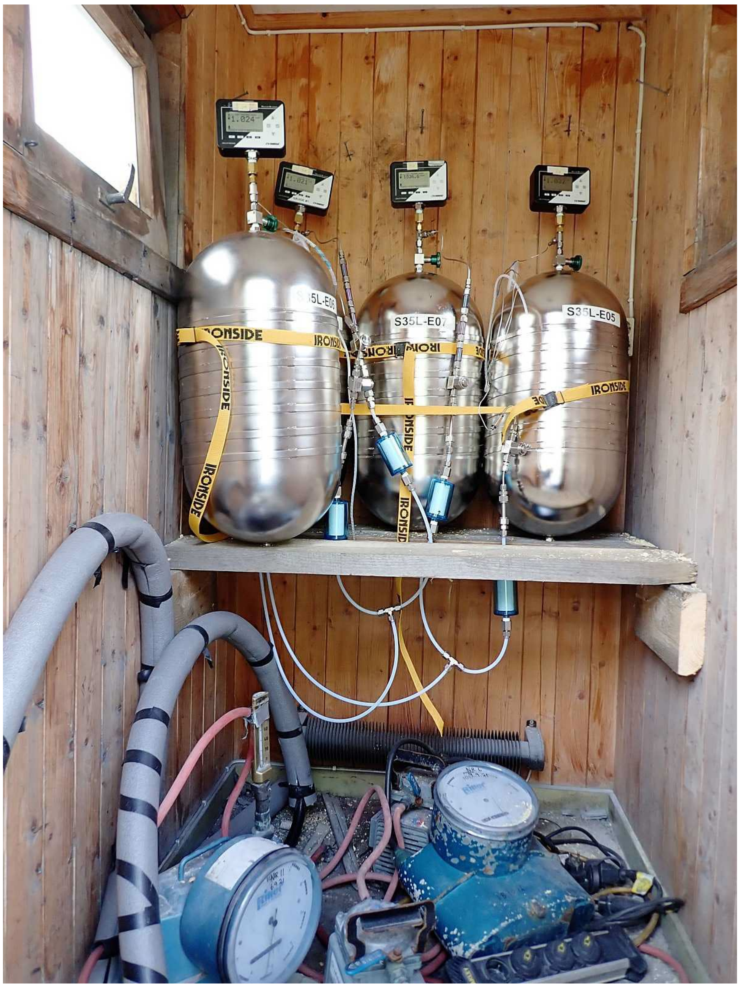

Figure 4: One inlet line from each of the chimneys was split to both CSIRO and NILU restrictor

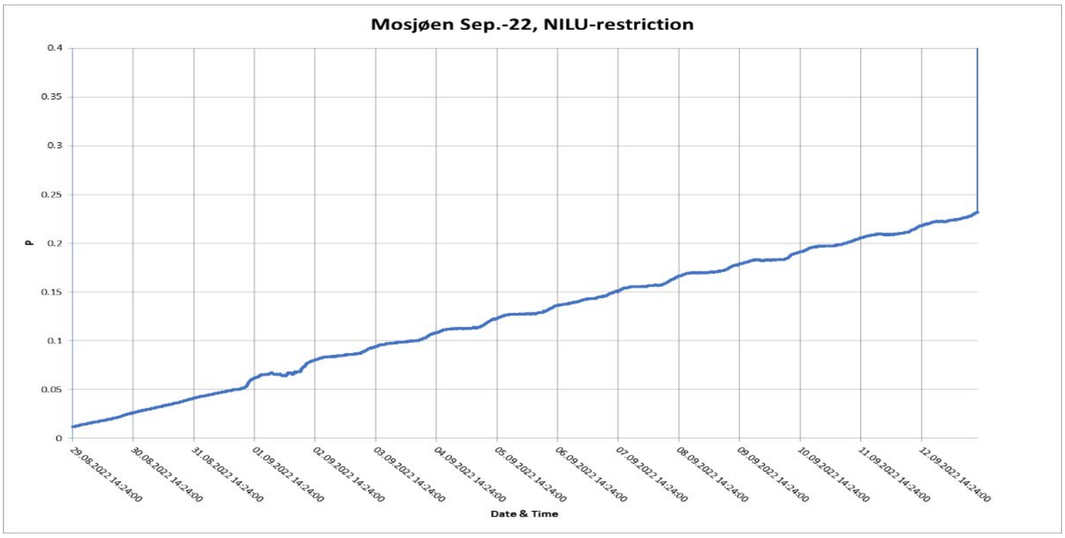

Figure 5 Tank pressure during 2 weeks sampling with NILU restrictors at stack 1B .Small fluctuations are due to change of temperature and atmospheric background pressure

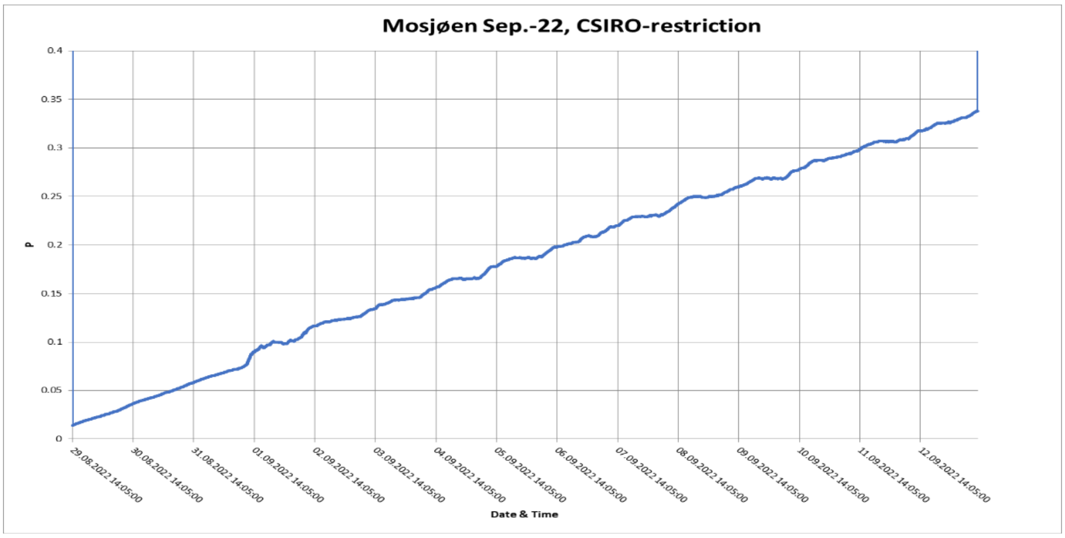

Figure 6 Tank pressure during 2 weeks sampling with CSIRO restrictors at stack 1B

Both samplers performed quite linear within the 14 days of sampling

Each canister was measured twice for 4 PFC species – sample E07 showed signs of leakage right from the start on august 29 due to a damaged main shut off valve of the canister and was not analysed further.

Sample ID	CF_4	C_2F_6	C_3F_8	c-C_4F_8
E05 CSIRO West	92.11	4.90	0.33	2.22
E05 CSIRO West	91.82	4.83	0.37	2.18
E07 NILU West	Valve malfunction on tank E07			
E06 CSIRO East	89.42	4.75	0.37	1.33
E06 CSIRO East	89.04	4.65	0.37	1.45
E08 NILU East	92.37	4.89	0.36	1.79
E08 NILU East	92.57	4.91	0.32	1.82

Table 1: Analysis results, all values are ppbv.

The results showing good repeatability as well as no major differences between the different restrictors (CSIRO -NILU)

4 Outlook

Overall, the results of the project on both Hydro's and Alcoa 's plants are very encouraging. The methods for time-integrated sampling and off-line Medusa GC-MS analysis are promising. There are still some issues to work on – like the final decision on size and design of the HF-scrubber. While other issues were solved– like the prevention of clogging the air flow during stack sampling. Sampling at other sites than the stack, for example on the roof top or at cell level, did not reveal any problems.

NILU is confident in finding good solutions for those issues and that "true" emission values could be obtained from long-time-integrated stack-sampling combined with offline analysis. Time periods of one month could be sampled with a canister size of about 15L and a flow rate of 0.1 ml/min.

Measurements at individual cell outflow can be performed with short time-integrated sampling ranging from minutes to several hours in order to monitor PFC emissions from conventional High Voltage Anode Effects (HVAE) (>8 V or 10 V) or Low-Voltage Anode Effects (LVAE)

Time-integrated sampling of airflows leaving the top of the halls will give a good indication of the diffusive emissions within the halls. Those emissions will vary in time, but will all in all be much closer to atmospheric background levels over long time periods. For those mixing ratios, FTIR or Quantum Cascade Lasers are not suitable. Offline sampling and GC-MS would be far superior and cheaper compared to quite insensitive online measurements.

The total cost of sampling and off-line analysis will be very competitive compared to long-time online measurements using FTIR or QCL. The sampling could be performed by the staff – not involving expensive site visits by NILU personnel. Such measurements could be done at all stacks at the same time and over the same time periods

5 References

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NILU
P.O. Box 100, NO-2027 KJELLER, Norway

E-mail: nilu@nilu.no
http://www.nilu.no

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