university of groningen | energy and sustainability research institute groningen | centre for isotope research

Photography encouraged

Instrument development for better observation of anthropogenic emissions of COS in the Netherlands

Steven van Heuven[1], Linda Kooijmans[2], Andrea Scifo[1], Bert Scheeren[1], Maarten Krol[1], and Huilin Chen[1]

(1) Centre for Isotope Research, Energy and Sustainability Research Institute, University of Groningen, Groningen, The Netherlands. (2) Meteorology and Air Quality Group, Wageningen University, Wageningen, The Netherlands . (s.m.a.c.van.heuven@rug.nl)

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No. 742798

Abstract

We developed a mobile analysis system for COS around a dual-QCL TILDAS featuring fast response at acceptable precision even for small samples. The system allows for automated switching between multiple samples (at varying pressures), with exacting pressure matching prior to switching. This newly developed instrument brings advancements in the ability to measure small-volume air samples, in a well-calibrated and easily repeatable manner. Integrated logging, semi-automated reading, processing and calibration workflow in MATLAB allows for rapid conversion of raw data into clibated output. We present early appliciation results.

Introduction

Dual-QCL (Aerodyne Research Inc., MA, USA), multi-species direct absorption spectrometer:

- 6 gases: COS, CO_2, CO, CH_4, N_2O, H_2O
- low volume cell (150 ml; V_{eff} @50 Torr: 10 ml)
- 36 m path length (+1.4 m purguable pre-path)
- pressure control is very precise, but very slow
- handling sensitivity: manual calibration iffy
- for AirCore: slow P-control: loss of profile top

Build frontend to alleviate!

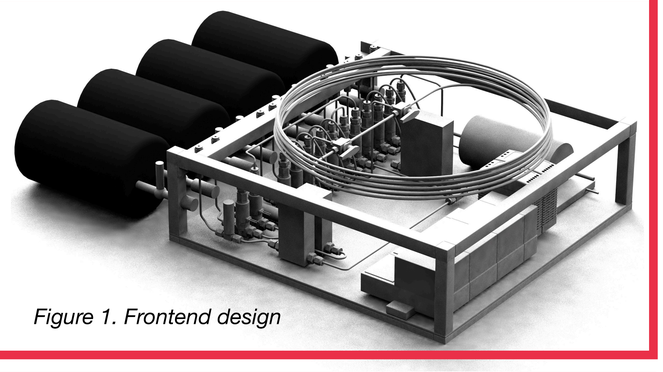


Figure 1. Frontend design

Frontend design

Home-built frontend:

- 1x N_2 (with built-in Aeronex purifier)
- 4x high-P samples (cylinders)
- 4x low-P samples (flask, lines)
- 1x AirCore (Karion et al., 2010)
- arbitrary sequencing, programable
- pressure-matching between samples
- instantaneous switching
- line purging for aircore
- line evacuation for flask samples
- PLC-control with intuitive UI
- UI on Aerodyne PC
- Data sync. with Aerodyne data
- small (50x50x15 cm),
- easy access
- Simulates AirCore filling
- No need for overblow
- AirCore connections purgeable
- Sample connections evacuable

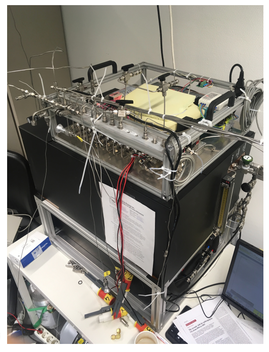
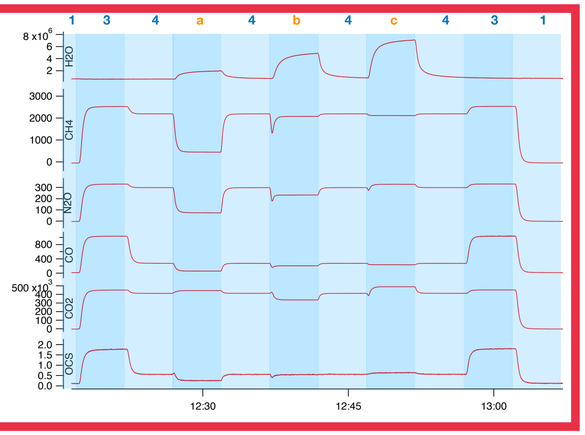


Figure 2. Frontend on QCL during testing and validation

Workflow

- Run sequence of cyl's (1-5) + samples (a-d):
  e.g., 134a4b4c4a4b4c431
- do curvefits, find asymptotes, get statistics
- interpolate standard in time
- for every sample get cal. coeffs from interp'ed stds
- calibrate samples to scale of stds.

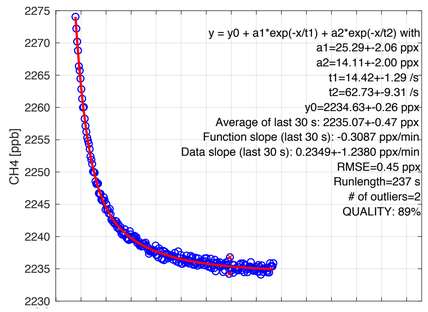
Figure 3. Example of QCL putput, showing concentrations of each of 6 measured gases (units: ppb) while stepping between 3 working standards (1,3,4) and 3 flask samples (a,b,c). Note that the three flask samples were not dry.



Performance

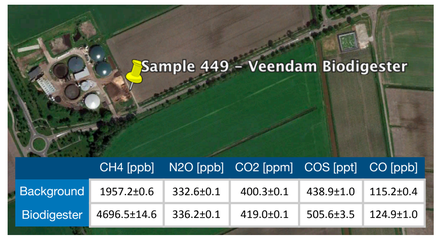
Typical flask analysis duration (4 samples, 3 standards, 1 target, 3 repeats): 2.5 hours. Flask sample precision and accuracy:
CH_4: ±0.3, <0.5 ppb / N_2O: ±0.05, <0.1 ppb / CO_2: ±0.05, <0.1 ppm / COS: ±6, <15 ppt / CO: ±0.8, <1.2 ppb

Figure 4. Example of QCL putput, showing concentrations of each of 6 measured gases (units: ppb) while stepping between 3 working standards (1,3,4) and 3 flask samples (a,b,c). Note that the three flask samples were not dry.



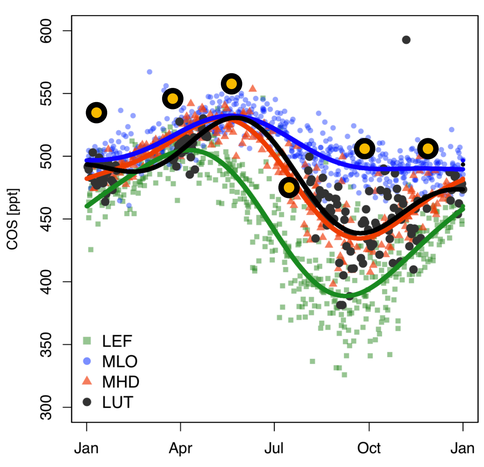
First application results

A). Samples collected downwind of a large-scale biodigester near village of Veendam, NL show strong enhancement of all gas species relative to background (i.e., upwind samples).

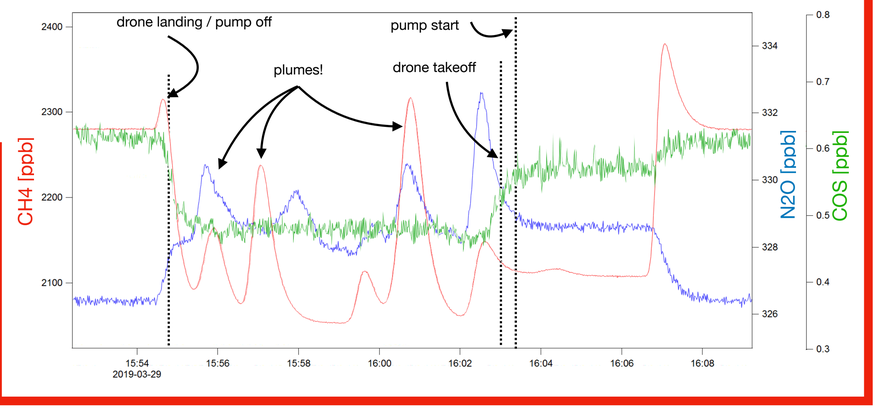


	CH4 [ppb]	N2O [ppb]	CO2 [ppm]	COS [ppt]	CO [ppb]
Background	1957.2±0.6	332.6±0.1	400.3±0.1	438.9±1.0	115.2±0.4
Biodigester	4696.5±14.6	336.2±0.1	419.0±0.1	505.6±3.5	124.9±1.0

B) Kooijmans et al. (2016) present the first measurements of COS on flask samples collected at the Lutjewad observatory, a coastal site in the Northeast of the Netherlands. We intend to extend that timeseries. Some 50 samples collected at Lutjewad in the period 2017-2019 are currently awaiting analysis, and more will be collected on a regular basis. Figure 6 (right) presents results of the first such measurements overlaid on the seasonal cycle presented by Kooijmans et al (2016).



C) First analysis of an 'Active AirCore' (Andersen et al., 2018), collected at a dairy farm in Grijpskerk (NL) on March 29th, 2019. The drone flight path of evidnetly insected the plume of CH_4 from dairy farm, a near-coincident plume N_2O from an active release. No COS enhancement above background levels is detected (note: figure presents uncalibrated data)



References

Andersen, T., Scheeren, B., Peters, W., and Chen, H.: A UAV-based active AirCore system for measurements of greenhouse gases, Atmos. Meas. Tech., 11, 2018.

Karion, A., Sweeney, C., Tans, P., and Newberger, T., AirCore: An Innovative Atmospheric Sampling System, Journal of Atmospheric and Oceanic Technology, 2010.

Kooijmans, L. M. J., Uitslag, N. A. M., Zahniser, M. S., Nelson, D. D., Montzka, S. A., and Chen, H.: Continuous and high-precision atmospheric concentration measurements of COS, CO2, CO and H2O using a quantum cascade laser spectrometer (QCLS), Atmos. Meas. Tech., 9, 2016.

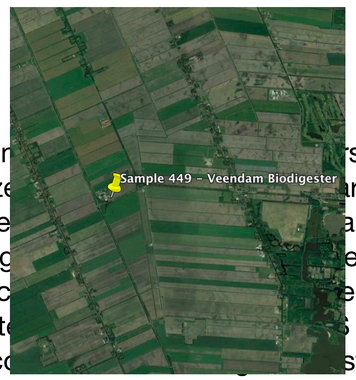
Aerodyne QCL

Dual laser, multi-species direct absorption spectrometer
– 6 gases: COS, CO2, CO, CH4, N2O, H2O
– low sample flow rate (~50 ml/min)
– low volume cell (~150 ml) (at 50 Torr: 10 ml effective)
– 36 m path length (+ 1.4 m purguable ambient path)
– pressure control is very precise, but very slow (…)

Possible applications:
– flasks, cylinders, AirCore, tower samples

But…
– sensitivity to handling means uncertain calibration
– slow pressure control means loss of top-of-profile

Build frontend to alleviate!



TODO:
- assign r rs (N2O from Lutjewad)
- optimize rly to improve throughput).
- conside amples in calibration (now “all are good”)
- test targ ed values for 3)
- derive c entration
- characte s vs CH4, and compensate (?)
- make co stability