

MEDUSA-GC/MS SOLUTION, THE MOST RECENT CRYOTECHNOLOGY APPLIED TO THE CONTINUOUS ANALYSIS OF CLIMATE-ALTERING SUBSTANCES IN AIR SAMPLES

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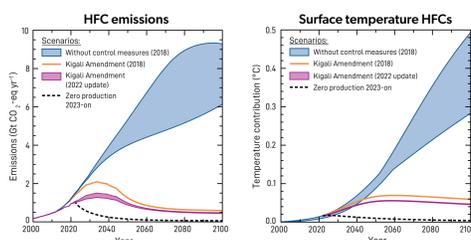
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INTRODUCTION

Emissions of greenhouse gases (GHGs) reported by countries in their GHG inventories to UNFCCC (United Nations Convention on Climate Change) represent the central information used in international policies to curb global GHG emissions in order to meet the targets of the Paris Agreement on climate change. To verify the implementation of the several treaties involving the reduction on use of HFCs - such as the Kigali Amendment to the Montreal Protocol (2016), the EU F-gas regulation (2014), and the EU-MAC directive (2006) - results based on reliable and continuous atmospheric observations are crucial. Fluorinated halocarbons are potent GHGs (GWPs to ~24000) whose concentration are expected to continue growing in the future; but are challenging compounds due to their extreme high volatility and the very low atmospheric concentrations.

Here we present results based on atmospheric observations made at the WMO GAW (World Meteorological Organisation Global Atmosphere Watch) station of Monte Cimone ISAC-CNR (CMN) in the frame of the AGAGE (Advanced Global Atmospheric Gases Experiment) network based on MEDUSA system, the newest cutting-edge instrumentation available from Markes.



References: World Meteorological Organization (WMO). Executive Summary. Scientific Assessment of Ozone Depletion: 2022

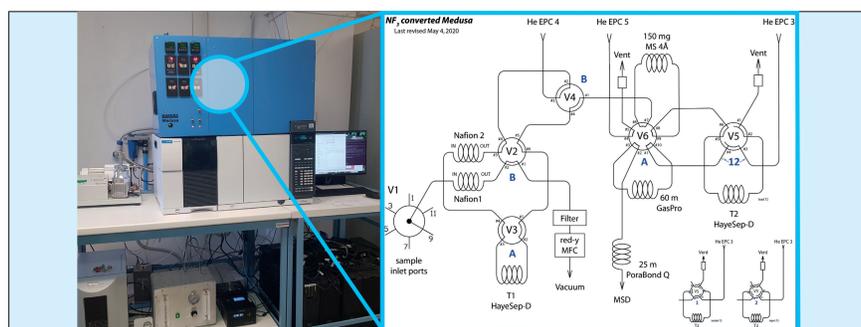


GOALS

- Provide efficient preconcentration and separation of a variety of compounds in the ppq-ppt range from the more abundant atmospheric components and bulk gases
- Provide a reliable and autonomous device for continuous and unattended operations in remote station
- Guarantee comparability and continuity with existing instrumentation and extend the measurement capability to most challenging compounds (NF₃ b.p. -129°C, CF₄ b.p. -128°C, SF₆ b.p. -64°C).

EXPERIMENTAL

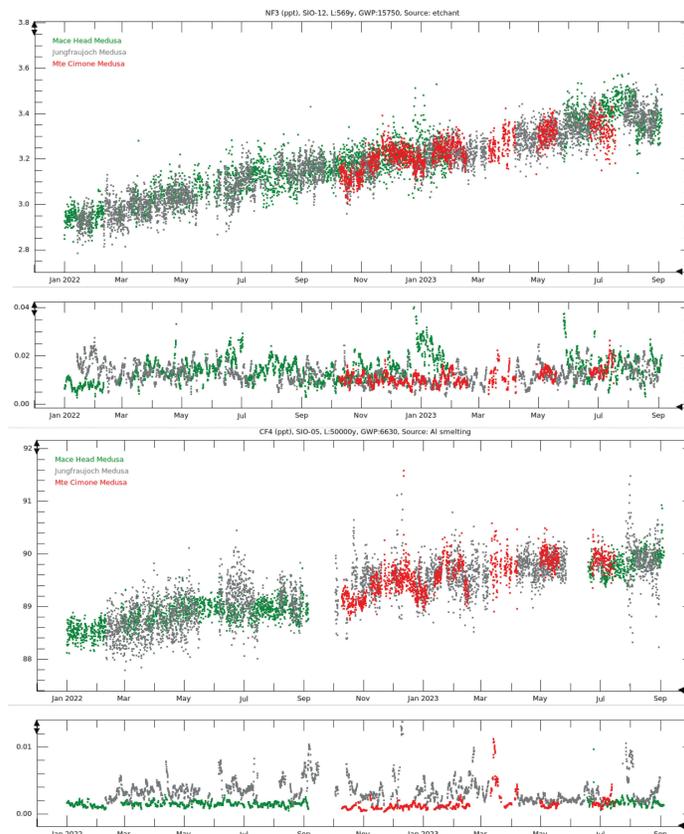
	Medusa	TD Markes Unity 2
Preconcentration	Dual trap, Hayesep D, 100/120 mesh	Multibed Ozone Precursor trap
Preconcentration Temp	-160 °C (Stirling cooler)	-35 °C (Peltier)
De-humidification	Nafion membrane tube	Nafion membrane tube
Chromatographic separation	Restek MolSieve 4A (150mg, 1/8"SS) + Agilent GasPro 60m, 0.32mm + Agilent PoraBondQ, 25m, 0.32mm	Agilent GasPro 60m, 0.32mm
Hardware	Agilent GC 7890B MSD 5977B	Agilent GC 6850 + MSD 5975C
Calibration	Whole air standard tank calibrated at SIO - University California, San Diego for the AGAGE network	
Sampling	Every second hour from a common SS/Pyrex inlet; 2l on Medusa, 1l on Unity2, by a KNFN86 pump, positive pressure, bracketed with working standard run	



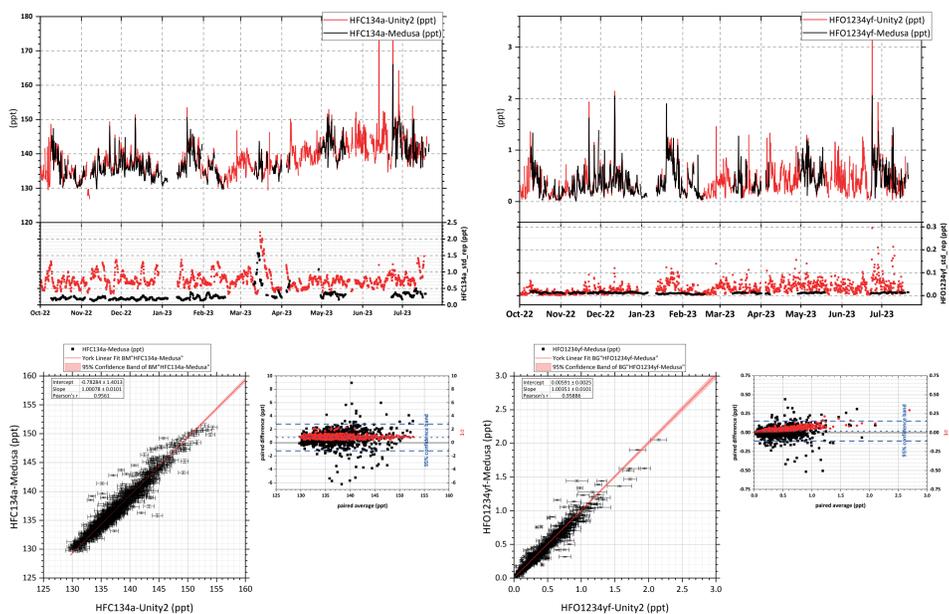
RESULTS

Comparison of the timeseries after 8 months of measurements:

- NF₃ and CF₄ against two European Medusa operating stations within the AGAGE network: Mace Head (Bristol University, UK and Galway University, IE) and Jungfraujoch (EMPA, Swiss)



- Comparison against UNITY2 setup for some of the common compounds



CONCLUSIONS

- high volatile compounds such as NF₃ and CF₄ alongside over 40 other halogenated compounds, such as Bromoform (b.p. +149°C) can be quantitatively trapped for volume up to 4 L
- bulk gas and other major components in real atmospheric samples are efficiently removed avoiding and minimizing possible interferences
- detection limit is in the range of ppq (fmol/mol) with precision (1s) lower than 1% for almost all the halogenated compounds and light hydrocarbons, 2% for NF₃.
- precisions for the most of the compounds is in the range of than
- the entire system has full programmability, versatility, and ease of operation to allow complete control of the variables involved in every step of the analytical method
- system is full automated and can operate continuously and unattended

REFERENCES

- World Meteorological Organization (WMO). Executive Summary. Scientific Assessment of Ozone Depletion: 2022
- Miller, et al. Medusa: a sample preconcentration and GC-MSD system for in situ measurements of atmospheric trace halocarbons, hydrocarbons and sulfur compounds, *Anal. Chem.*, 80, 1536-1545, 2008
- Prinn, et al. History of chemically and radiatively important atmospheric gases from the Advanced Global Atmospheric Gases Experiment (AGAGE), *Earth Syst. Sci. Data*, 10, 985-1018, 2018

