WP2 First time isotope ratio gas reference materials for $\delta^{13}CH_4$ and $\delta^{2}H\text{-}CH_4$

Status report & upcoming activities

Stefan Persijn (VSL) on behalf of all WP2 partners

Stakeholder catchup Stellar, 26 February 2021

Dutch Metrology Institute

NPL, MPG, RUG, AL, JSI, Empa, UEF, INRIM, TUBITAK

WP2 First time isotope ratio gas reference materials for $\delta^{13}CH_4$ and $\delta^2H\text{-}CH_4$

Aim

Provide CH_4 reference materials linked to the … o scales.

Current status

Interlaboratory comparison of δ^{13}C and δD measure… atmospheric CH_4 for combined use of data sets from different laboratories

Taku Umezawa[1,2], Carl A. M. Brenninkmeijer[1], Thomas Röckmann[3], Carina van der Veen…

… t offsets of δ^{13}C-CH_4 and δD-… ata sets reported from differ-… s among laboratories at mod-… read over ranges of 0.5 ‰ for … CH_4. The intercomparison re-

https://doi.org/10.5194/amt-11-1207-2018

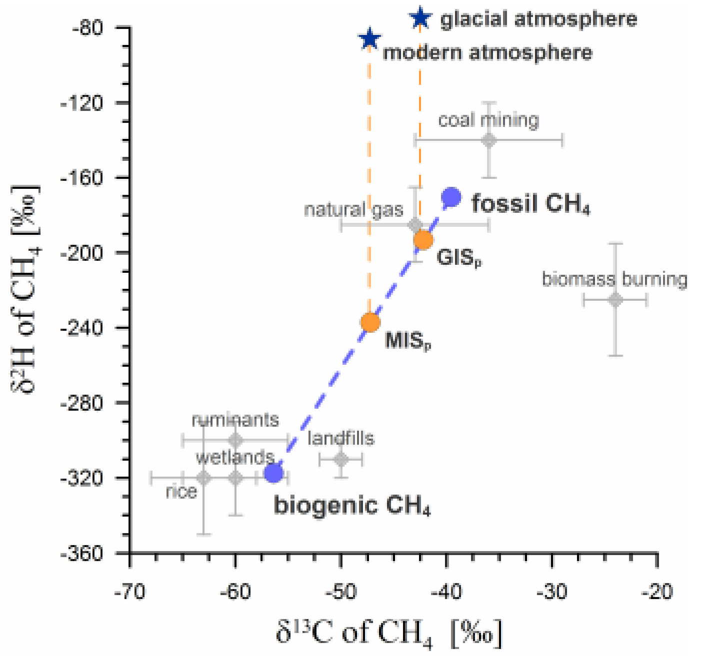


Fig. 1. Dual isotope signatures of CH_4 for δ^{13}C and δ^2H. Grey diamonds mark the field of δ^{13}C and δ^2H isotopes of CH_4 according to its source (Quay et al., 1999). Blue circles indicate δ^{13}C and δ^2H pairs of the parental CH_4 gases (fossil and biogenic CH_4). Based on our fossil and biogenic CH_4, we can produce filial CH_4 mixtures with δ^{13}C and δ^2H isotope values that fall on the dashed blue mixing line. The two filial CH_4 gas mixtures are indicated by orange circles where GIS_p and MIS_p represent the δ^{13}C of glacial and modern atmospheric samples, respectively. Isotope signatures of glacial and modern atmospheric CH_4 are indicated by the dark blue stars.

Source: Sperlich et a.., 2012

Project will provide

To develop gas reference materials of methane (pu… with a repeatability of 0.02 ‰ for δ^{13}C-CH_4 and 1 ‰ for δ^2H… ‰ for δ^{13}C-CH_4 and 5 ‰ for δ^2H-CH_4, ensuring traceability t… ility of more than one year.

Dutch Metrology Institute

Task 2.1: Inventory of source and supply and development of pure methane gas reference materials

Aim: to identify commercially available pure CH_4 relevant for underpinning atmospheric measurements for source apportionment. Pure CH_4 will be used to prepare gas reference materials of pure CH_4.

Isotope	Range suggested	Target repeatability	Target uncertainty
$\delta^{13}C\text{-}CH_4$	-20 ‰ to -80 ‰	0.02 ‰	0.2 ‰
$\delta^{2}H\text{-}CH_4$	-75‰ to -400 ‰	1 ‰	5 ‰

Key challenges:

- find proper cylinder passivation to enable long term stability and minimise fractionation
- a full understanding of the major contributors to the uncertainty budget
- high precision IRMS measurements to achieve traceability to the scales with low uncertainty

VSL, NPL, AL, MPG, JSI, RUG

Start: Sep 2020

Task 2.2: Diluted $\delta^{13}CH_4$ and $\delta^{2}H\text{-}CH_4$ in air gas reference materials

Aims:

1) to prepare ≥3 reference gas mixtures of CH_4 in a CH_4-free air matrix at 1.85 μmol mol^{-1} with different isotopic composition, of which the isotope ratios and amount fractions have assigned values. Prepared by gravimetry in high pressure cylinders with same challenging target uncertainty as the pure CH_4 and ≥1 year stability

2) fully characterize the zero-air used in the preparation to study the influence on fractionation of the purification process used to remove methane.

3) to prepare diluted CH_4 reference materials in different matrix gases and at different amount of substance fractions to support research in WP3 towards novel calibration approaches and to study the influence of matrix gas changes on the uncertainty using spectroscopy.

VSL, NPL, AL, Empa, MPG, JSI, UEF, RUG

Start: June 2021

Task 2.3: Linking to the $\delta^{13}C\text{-}CO_2$ reference materials for an independent assessment of the accuracy and uncertainty of $\delta^{13}C\text{-}CH_4$ reference materials

Aim: to compare the $\delta^{13}C\text{-}CH_4$ reference materials to the $\delta^{13}C\text{-}CO_2$ reference materials to provide an independent assessment of the accuracy and uncertainty claims. A facility will be developed for the conversion of CH_4 to CO_2 and the sensitivities and contribution to uncertainty of this process will be fully characterised. The target uncertainty is 0.1 ‰ for $\delta^{13}C\text{-}CO_2$.

NPL, INRIM, TUBITAK, RUG, MPG

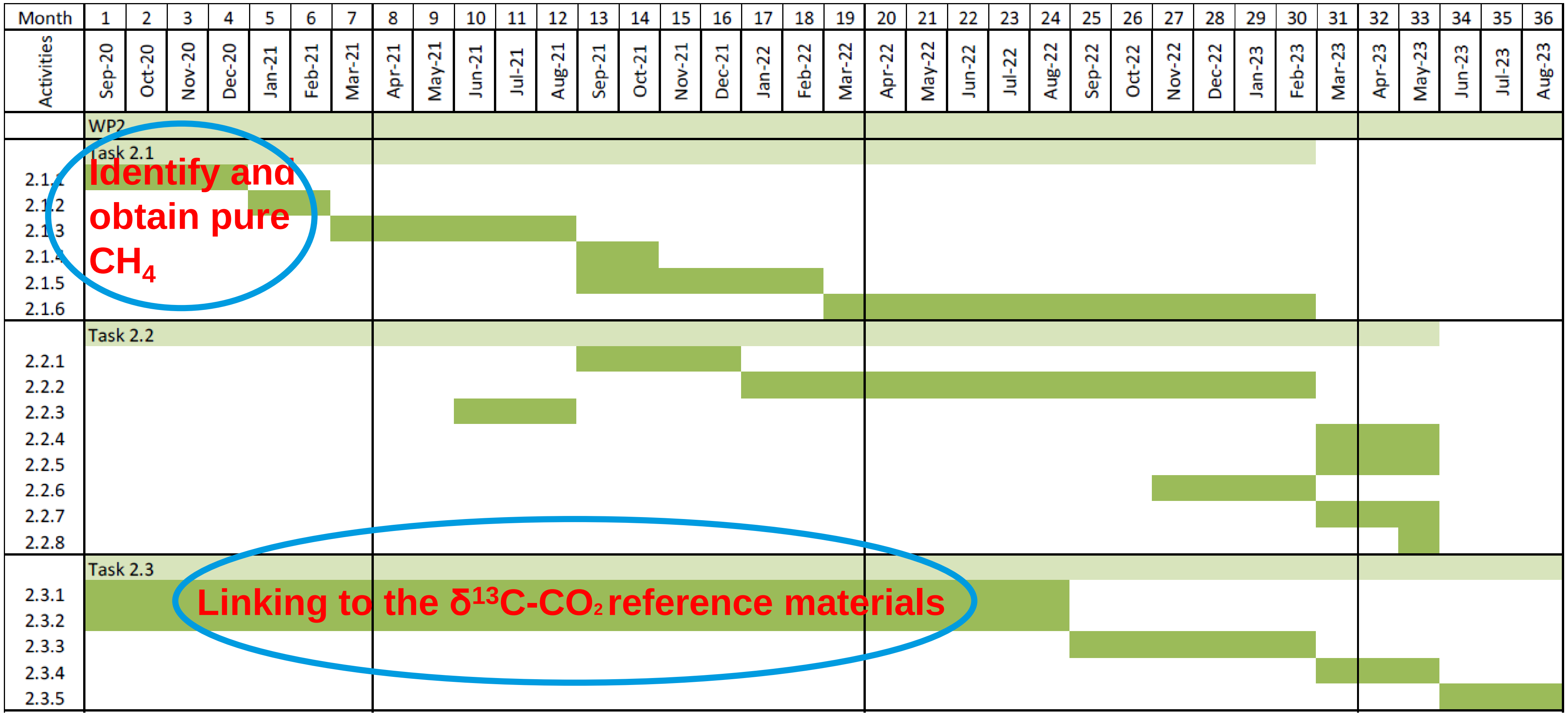
Start: Sep 2020

Time line

Pure CH_4 gas standards

CH_4 gas standards at ambient levels

Link WP1-WP2



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Composition measurements of biogas

Main molecular composition (in mol%) of investigated biogas samples and natural gas samples

Determined d13C-IRMS values of biogas CH_4 fractions and natural gas samples after combustion to CO_2.

Biogas	CH_4 (mol%)	CO_2 (mol%)	C_xH_y (mol%)	(N_2, O_2 ,..) (mol%)	$\delta^{13}C$ (‰)
Maize_onions	56,3	42,2	0,02	1,5	-55,6
Landfill_1	61,1	32,1	0	6,8	-61,2
Organic waste	61,5	38,4	0	0,2	-52,0
Cookies_fish	85,2	12,0	0	2,8	-53,6
Mun. sewage sludge	89,5	10,3	0	0,3	-28,6
Landfill_2	54,4	30,5	0	15,1	-56,3
Sugar beet	87,8	8,2	0	4,1	-39,2
Manure_vegetables	59,6	35,8	0	4,7	-48,4
Manure_meat waste	96,4	3,3	0	0,4	-57,2
Natural gas					
Norway gas	87,1	2,06	8,9	1,95	-39,9
North Sea gas	85,07	2,66	4,93	7,34	-29,8
Groningen gas	81,05	1,02	3,45	14,48	-28,4

sources:

Palstra, S. W. L. and Meijer, H. A. J.: Biogenic Carbon Fraction of Biogas and Natural Gas Fuel Mixtures Determined 2014. with C-14, Radiocarbon, 56(1), 7–28, doi:10.2458/56.16514,

Palstra, S.W.L., et al. EMPIR project '16ENG05 Metrology for Biomethane' WP3.7 final report

university of groningen

VSL activities to obtain pure CH_4

Fossil

High purity CH_4 (5.5 purity) from fossil origin is available.

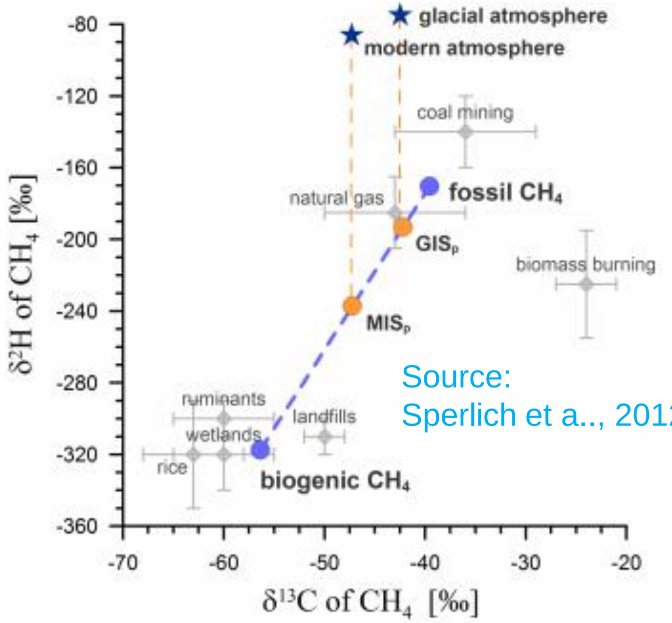
Biogenic

Consulted other NMI's and several companies and organizations.

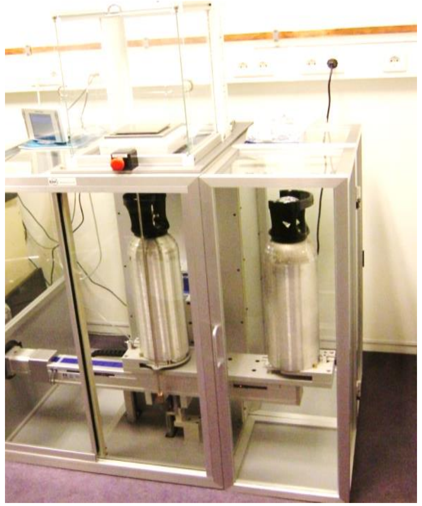
Feedback: CH_4 from Bio-CNG or Bio LNG seem good candidates with respect to low levels of impurities and the required pressure.

Some producers were contacted. Status:

- 1 x required volume too small
- 1 x facility will become available later this year
- 2 x still under discussion



Source:
Sperlich et a.., 2012



Activities

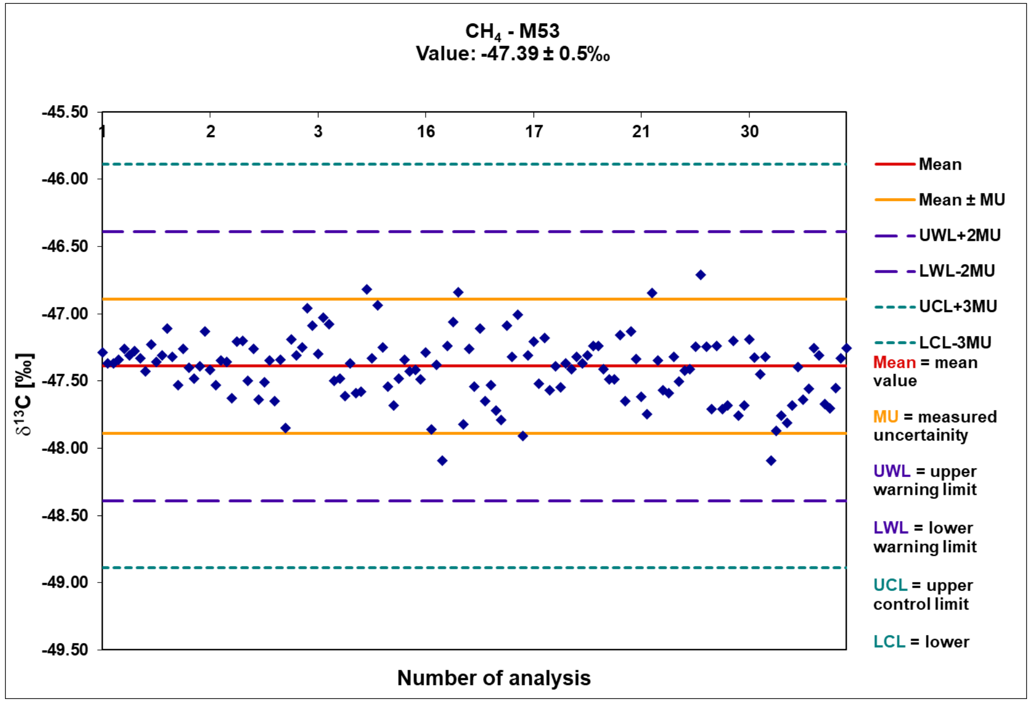
Available methane sources in Slovenia

Provider	Purity	Cylinder volume [L]	Pressure [bar]	Source	Isotopic composition
Messer	4.5 5.5	50	200	Synthetic	Unknown
Istrabenz (SIAD)	2 2.5 3.5 4.5 5.5 1.7 (fossil gas)	10 20 40 (1 L higher purities only)	200 (1 L: 150)	Natural	$\delta^{13}C$ ≈ from -40 to -60‰ $\delta^{2}H$ is unknown
GTG (Linde)	3.5 4.5 5.5	2 (except 3.5) 10 50	200 (2 L: 100)	Unknown	Unknown
TPJ	3.5 From pipeline	50	200	Synthetic	Unknown

Activities

Methane measurements on Europa Scientific 20-20 IRMS with ANCA TG

	Repr.	Bias				
	$u(R_w) = S_{RW}$	Ref value	*U* (*k*=2)	u_c	Lab result	$bias_i$
M53	0.26	-47.39	0.5	0.25	-47.41	-0.02
					Če je samo en CRM:	
		u(Cref)	RMS_{bias}	n	s_bias	*u*(bias)
		0.25	0.02	166	0.2554511	0.251569
Result:						
u_c =	0.36 ‰					
U (*k*=2) =	0.72 ‰					



Further activities:
optimization of the δ^{13}C determination in CH_4 using EA/IRMS
establishment of the system for δ^2H and δ^{13}C determination in CH_4 by EA/TC/IRMS (Sperlich et al., 2016; 2020)

Jožef Stefan Institute

Air Liquide progress in WP2

1.- Pure gases N_2, O_2 & Ar 50 L 200 bar

- 12 cyl N2 + 3 cyl O2 + 1 Cyl Ar sent to NPL Nov 2020
- 14 cyl N2 waiting for sending to NPL in the Spanish custom
- 8 cyl N2 + 1 cyl O2 waiting in Air Liquide for sending to VSL

2.- Pure CH_4

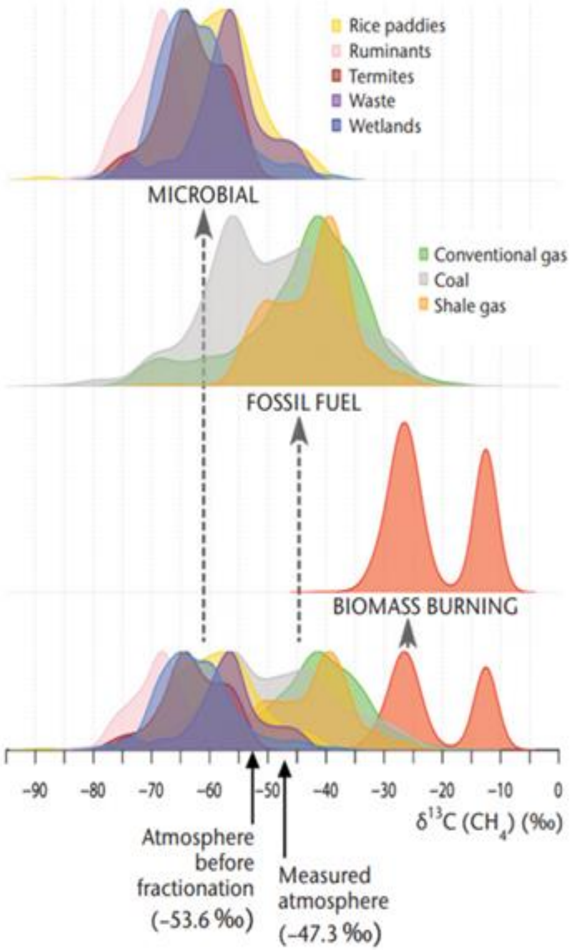
- Two cylinders from same lot 99,999% purity Air Liquide production (fossil source):
  - 1 cyl waiting for sending to NPL in the Spanish custom
  - 1 cyl waiting in Air Liquide for sending to VSL
- One sample of CH4 sent to Max-Planck (Heiko) for isotope ratio analysis.
- Looking for other possible CH4 sources. Not found until now: purity and pressure not enough.

3.- Empty cylinders with internal treatment

- **26 B10 l cyl prepared and waiting for sending to NPL in the Spanish custom (NPLvalve)**
- **20 B05 l and 2 B10 l cyl with DIN-1 or UNI 11144-5 valves for VSL, TUBITAK and INRIM in preparation for Aculife III Megalong treatment**
- **2 B10 l cyl with Aculife IV prepared and waiting for sending to VSL.**

Task 2.1/2.2 CH_4-in-air gas reference materials

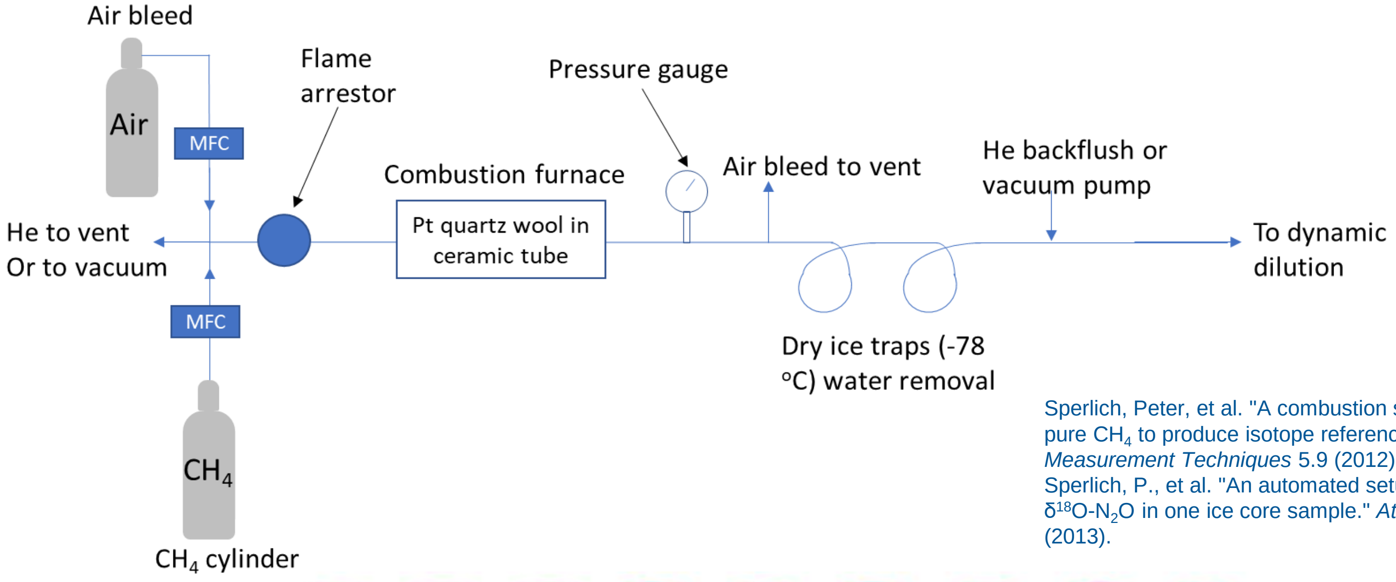
- Obtained one pure CH_4 fossil source, awaiting assignment of $\delta^{13}C$-CH_4 and δD-CH_4 at Max Planck iso-lab. NPL have a second CH_4 source with a $\delta^{13}C$-CH_4 of near measured ambient $\delta^{13}C$-CH_4. Still searching for a biomethane source and investigating spiking to achieve full range.
- Developed preparation plan for the dilution of pure CH_4 to 650 µmol mol^{-1} and 1.95 µmol mol^{-1} in synthetic air with the lowest gravimetric uncertainty of 0.082 % k=1 for the ambient amount fractions
- Matrix gases - impurity analysis is underway of Ar, O_2 and N_2 for the Air Liquide matrix gases
- A full uncertainty budget is being prepared for the amount fraction of CH_4 reference materials with 1 µmol mol^{-1} Kr – is dependant on exact matric gas requirements for WP3



Task 2.3: Linking to the $\delta^{13}C$-CO_2 reference materials for an independent assessment of the accuracy and uncertainty of $\delta^{13}C$-CH_4 reference materials

A facility will be developed for the conversion of CH_4 => CO_2 and the sensitivities and contribution to uncertainty of this process will be fully characterised. The target uncertainty is 0.1 ‰ for $\delta^{13}C$-CO_2.

- Developing a CH_4 to CO_2 combustion facility based on literature by Sperlich *et al.*
- Design of a dynamic dilution of the CO_2 output to 410 µmol mol^{-1} using a two stage system based on mass flow controllers and mol blocs for direct measurement at 410 µmol mol^{-1} by CRDS.



Sperlich, Peter, et al. "A combustion setup to precisely reference $\delta^{13}C$ and $\delta^{2}H$ isotope ratios of pure CH_4 to produce isotope reference gases of $\delta^{13}C$-CH_4 in synthetic air." *Atmospheric Measurement Techniques* 5.9 (2012): 2227-2236.
Sperlich, P., et al. "An automated setup to measure paleoatmospheric $\delta^{13}C$-CH_4, $\delta^{15}N$-N_2O and $\delta^{18}O$-N_2O in one ice core sample." *Atmospheric Measurement Techniques Discussions* 6.1 (2013).

Thank you for your attention!

Any questions or remarks?

Contact: spersijn@vsl.nl