TÜBİTAK

UME

EMRP ENV52 HIGHGAS
Isotopic CO_2 reference standards

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Stakeholder Workshop

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Task 1.2

An investigation of systematic biases introduced from instrumentation at monitoring stations when reference gases vary in isotopic composition from the measured environment. (NPL, TUBITAK)

Focus will be on:

- Development of reference standards of CO_2 with varying isotopic composition
- Studying the influence of the variation in CO_2 isotopic composition between the reference standard and the measured sample on instrument response

Deliverable List

Deliverable number	Deliverable description	Participants	Deliverable type	Delivery date
1.2.1	Specification of a suite of at least 4 CO_2 mixtures with varying isotopic content	NPL	List	May 2015
1.2.2	Specification of the IRMS facility emailed to NPL	TUBITAK	Email	Jun 2015
1.2.3	Protocol describing the IRMS validation measurements planned for CO_2 mixtures	NPL	Protocol	Nov 2015
1.2.4	At least 4 reference standard mixtures of CO_2 with different isotopic compositions (covering at least a relative shift in the δ scale of 25 δ13C ‰) prepared by blending different amounts of $13CO_2$ with commercially available CO_2	NPL	Artefact	Jan 2016
1.2.5	Mixtures in D1.2.4 quantified for isotopic composition using IRMS	TUBITAK	Dataset	May 2016
1.2.6	Analytical bias related to CO_2 isotopic composition quantified for CRDS	NPL	Dataset	Nov 2016

Activities in 1.2.1

Task 1.2.1 : Specification of a suite of at least 4 CO_2 mixtures with varying isotopic content

Delivery Date : May 2015 (Completed)

Participants : NPL

- NPL has specified a suit of CO_2 mixtures which span a range of isotopic compositions. The CO_2 mixtures are summarised below:

CO_2 source	δ value	Concentration [ppm]				
Underground source	δ -1.38			400		
NPL blend	δ -5.25	360	380	400	420	440
Industrial source	δ -34.19			400		
Combustion source	?			400		
Fermentation source	?			400		

- NPL blend is blended from pure $^{13}CO_2$ and the industrial source CO_2
- NPL planned purchasing of a purely fermentation or combustion source

Activities in 1.2.2

Task 1.2.2 : Specification of the IRMS facility emailed to NPL

Delivery Date : June 2015 (completed)

Participants : TUBITAK

- Current IRMS facility used for determination of adulteration in commercially available honey samples*

IRMS Facility (Thermo Finnigan MAT 253)

*Adnan et *al.*, 13C/12C pattern of honey from Turkey and determination of adulteration in commercially available honey samples using EA-IRMS, Food Chemistry 130 (2012) 1115–1121,

Activities in 1.2.2

- Adaption of current IRMS facility for isotope gas measurements were examined
- A gas sampling unit was developed for the direct injection from the cylinders in gaseous phase

Auto gas sampling unit + GC-IRMS

Activities in 1.2.2 (cont'd)

- Search for isotope standards which will be used for testing purposes was carried out and the standards were purchased from NIST.

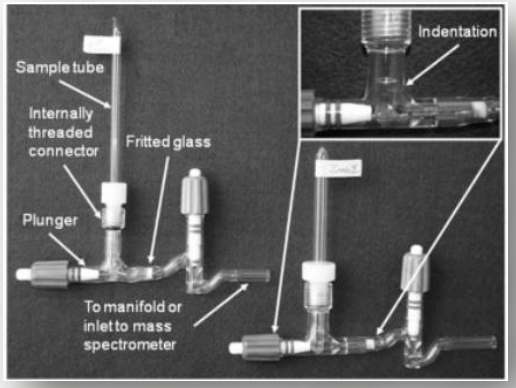
8564: CO_2-Biogenic, Modern Biomass Origin (Carbon Dioxide)

Table 1. Reference Values for $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$

Reference Material	$\delta^{13}C_{VPDB} \pm U^{(a)}$ (‰)	$\delta^{18}O^{n}_{VPDB} \pm U^{(a)}$ (‰)
RM 8562 (CO_2-Heavy)	–3.76 ± 0.07	–8.43 ± 0.44
RM 8563 (CO_2-Light)	–41.56 ± 0.09	–23.61 ± 0.48
RM 8564 (CO_2-Biogenic)	–10.45 ± 0.07	+0.06 ± 0.40

Activities in 1.2.2 (cont'd)

- A tube cracker to be able use these reference materials has been manufactured.



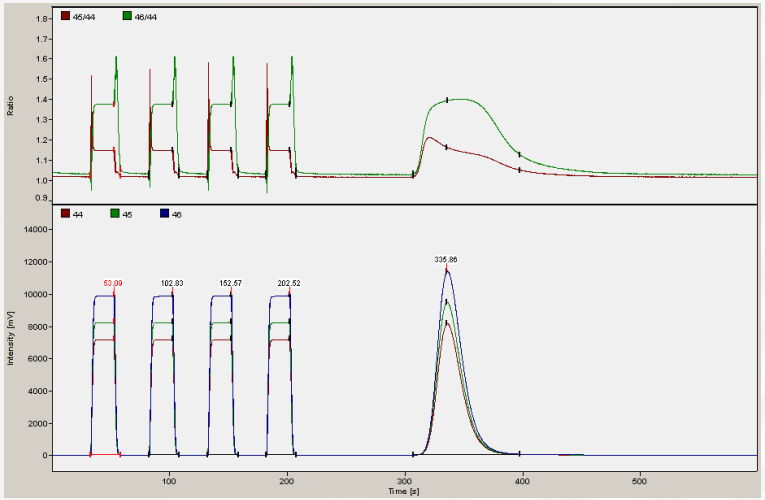
Rapid Commun. Mass Spectrom. 2010; 24: 3219–3220

Tube cracker at TUBITAK UME

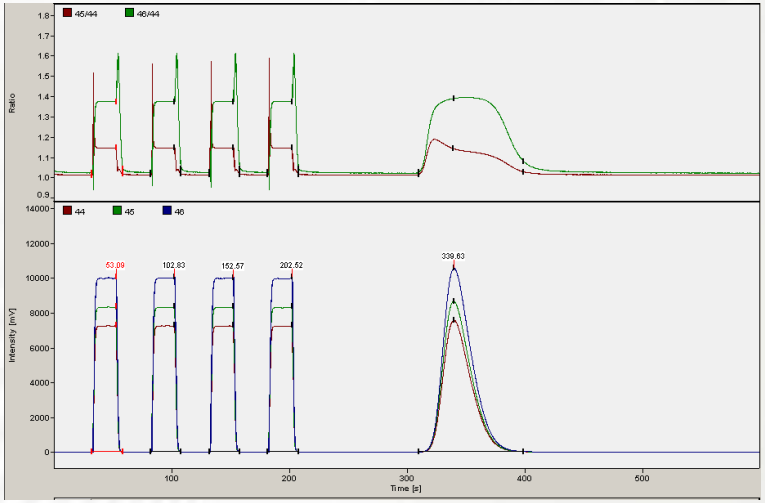
Activities in 1.2.2 (cont'd)

- Calibration of the working CO_2 gas used in IRMS

Ref. Mat.: NBS22 oil - $^{13}\delta$: -30.03



Ref. Mat.: LSVEC (Lithium Carbonate) - $^{13}\delta$: -46.6



Replicate	1	2	3	4	5	6	7	8	9	10	Total
$^{13}\delta$ (‰)	-41.428	-41.353	-41.44	-41.485	-41.393	-41.439	-41.317	-41.457	-41.385	-41.417	Average
	-41.422	-41.361	-41.447	-41.492	-41.407	-41.446	-41.314	-41.461	-41.392	-41.393	-41.4112
	-41.422	-41.367	-41.453	-41.487	-41.392	-41.446	-41.315	-41.457	-41.378	-41.396	SD
	-41.409	-41.359	-41.436	-41.494	-41.393	-41.43	-41.31	-41.466	-41.379	-41.411	0.051258
Average	-41.4203	-41.36	-41.444	-41.4895	-41.3963	-41.4403	-41.314	-41.4603	-41.3835	-41.4043	RSD
SD	0.008016	0.005774	0.007528	0.004203	0.007182	0.007588	0.002944	0.004272	0.006455	0.011587	0.123779

Replicate	1	2	3	4	5	6	7	8	9	10	Total
$^{13}\delta$ (‰)	-41.432	-41.982	-42.02	-41.149	-42.065	-41.395	-41.448	-41.146	-41.542	-41.822	Average
	-41.417	-41.993	-42.036	-41.169	-42.052	-41.394	-41.458	-41.142	-41.545	-41.825	-41.6027
	-41.447	-41.987	-42.042	-41.164	-42.052	-41.385	-41.453	-41.138	-41.535	-41.824	SD
	-41.44	-41.969	-42.041	-41.171	-42.063	-41.412	-41.454	-41.136	-41.544	-41.82	0.348111
Average	-41.434	-41.9828	-42.0348	-41.1633	-42.058	-41.3965	-41.4533	-41.1405	-41.5415	-41.8228	RSD
SD	0.012884	0.01021	0.010178	0.009946	0.006976	0.011269	0.004113	0.004435	0.004509	0.002217	0.123779

$^{13}\delta$ value of reference gas CO_2 :

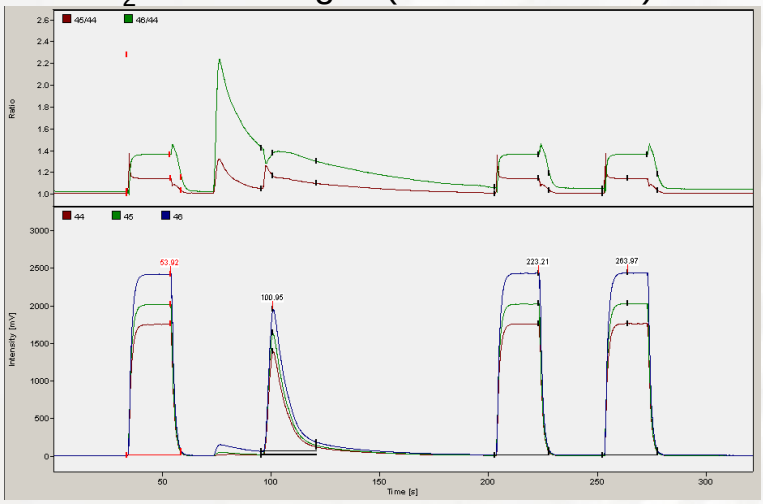
-41.507

Activities in 1.2.2 (cont'd)

- Preliminary gas analyses with gas injection trials

Column	HP-PLOT Q 30 m length, 0.53 mm I.D and 40 µm film thickness
Injection:	Splitless mode
Injection volume:	800 µL (syringe), 2 ml (autosampler)
Injection temp.:	200 °C
Carrier gas:	Helium, constant flow 10 mL/min.
Oven temp. program:	40 °C, 4 min

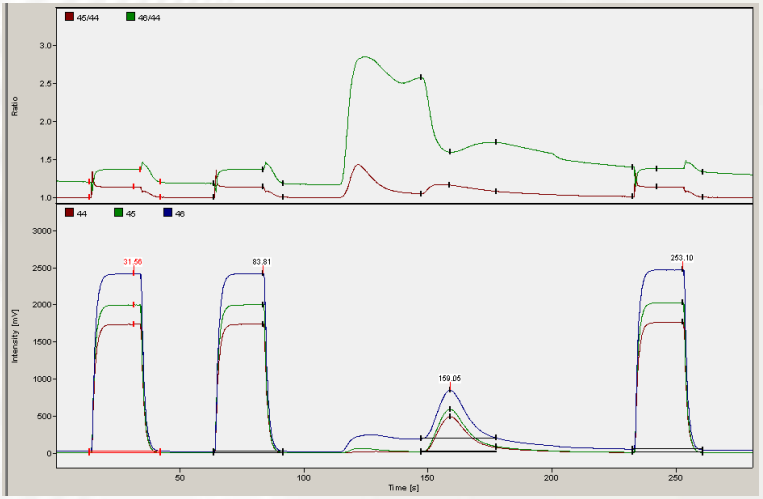
CO_2 reference gas (NIST RM 8564)



injection by syring

poor repeatability

400 ppm CO_2 – air mixture



Replicate	1	2	3	4	5	6
$^{13}\delta$ (‰)	-3,659	-3,362	-3,548	-3,626	-3,499	-3,732
Average	-3.571					
SD	0.131					
RSD %	3.674					

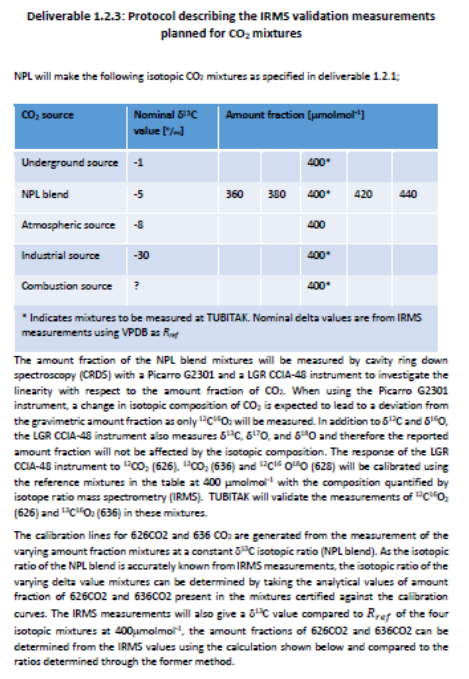
Activities in 1.2.3

Task 1.2.3 : Protocol describing the IRMS validation measurements planned for CO_2 mixtures

Delivery Date : November 2015 (Completed)

Participants : NPL

- The protocol has been prepared by NPL together with TUBITAK.



Deliverable 1.2.3: Protocol describing the IRMS validation measurements planned for CO_2 mixtures

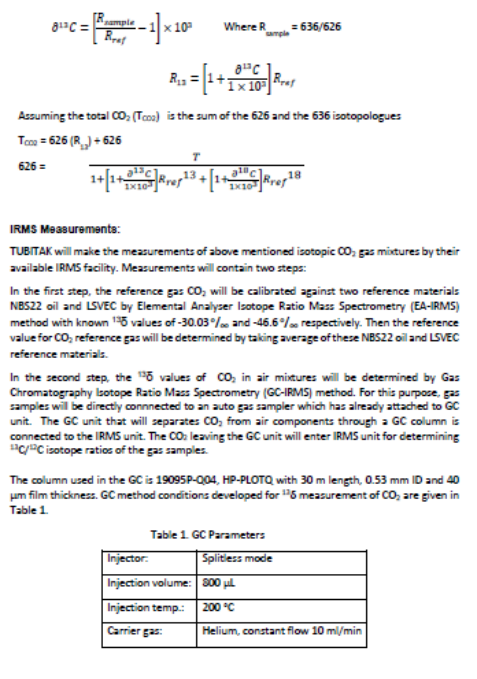
NPL will make the following isotopic CO_2 mixtures as specified in deliverable 1.2.1;

CO_2 source	Nominal $\delta^{13}C$ value [‰]	Amount fraction [μmolmol^{-1}]				
Underground source	-1			400*		
NPL blend	-5	360	380	400*	420	440
Atmospheric source	-8			400		
Industrial source	-30			400*		
Combustion source	?			400*		

* Indicates mixtures to be measured at TUBITAK. Nominal delta values are from IRMS measurements using VPDB as R_{ref}

The amount fraction of the NPL blend mixtures will be measured by cavity ring down spectroscopy (CRDS) with a Picarro G2301 and a LGR CCIA-48 instrument to investigate the linearity with respect to the amount fraction of CO_2. When using the Picarro G2301 instrument, a change in isotopic composition of CO_2 is expected to lead to a deviation from the gravimetric amount fraction as only $^{12}C^{16}O_2$ will be measured. In addition to $\delta^{13}C$ and $\delta^{16}O$, the LGR CCIA-48 instrument also measures $\delta^{13}C$, $\delta^{17}O$, and $\delta^{18}O$ and therefore the reported amount fraction will not be affected by the isotopic composition. The response of the LGR CCIA-48 instrument to $^{12}CO_2$ (626), $^{13}CO_2$ (636) and $^{12}C^{16}O^{18}O$ (628) will be calibrated using the reference mixtures in the table at 400 μmolmol^{-1} with the composition quantified by isotope ratio mass spectrometry (IRMS). TUBITAK will validate the measurements of $^{12}C^{16}O_2$ (626) and $^{13}C^{16}O_2$ (636) in these mixtures.

The calibration lines for 626CO2 and 636 CO_2 are generated from the measurement of the varying amount fraction mixtures at a constant $\delta^{13}C$ isotopic ratio (NPL blend). As the isotopic ratio of the NPL blend is accurately known from IRMS measurements, the isotopic ratio of the varying delta value mixtures can be determined by taking the analytical values of amount fraction of 626CO2 and 636CO2 present in the mixtures certified against the calibration curves. The IRMS measurements will also give a $\delta^{13}C$ value compared to R_{ref} of the four isotopic mixtures at 400μmolmol^{-1}, the amount fractions of 626CO2 and 636CO2 can be determined from the IRMS values using the calculation shown below and compared to the ratios determined through the former method.



$$\delta^{13}C = \left[\frac{R_{sample}}{R_{ref}} - 1\right] \times 10^3 \qquad \text{Where } R_{sample} = 636/626$$

$$R_{13} = \left[1 + \frac{\delta^{13}C}{1 \times 10^3}\right] R_{ref}$$

Assuming the total CO_2 (T_{CO2}) is the sum of the 626 and the 636 isotopologues

$T_{CO2} = 626\,(R_{13}) + 626$

$$626 = \frac{T}{1 + \left[1 + \frac{\delta^{13}C}{1\times10^3}\right] R_{ref}{}^{13} + \left[1 + \frac{\delta^{18}C}{1\times10^3}\right] R_{ref}{}^{18}}$$

IRMS Measurements:

TUBITAK will make the measurements of above mentioned isotopic CO_2 gas mixtures by their available IRMS facility. Measurements will contain two steps:

In the first step, the reference gas CO_2 will be calibrated against two reference materials NBS22 oil and LSVEC by Elemental Analyser Isotope Ratio Mass Spectrometry (EA-IRMS) method with known $^{13}\delta$ values of -30.03 ‰ and -46.6 ‰ respectively. Then the reference value for CO_2 reference gas will be determined by taking average of these NBS22 oil and LSVEC reference materials.

In the second step, the $^{13}\delta$ values of CO_2 in air mixtures will be determined by Gas Chromatography Isotope Ratio Mass Spectrometry (GC-IRMS) method. For this purpose, gas samples will be directly connnected to an auto gas sampler which has already attached to GC unit. The GC unit that will separates CO_2 from air components through a GC column is connected to the IRMS unit. The CO_2 leaving the GC unit will enter IRMS unit for determining $^{13}C/^{12}C$ isotope ratios of the gas samples.

The column used in the GC is 19095P-Q04, HP-PLOTQ with 30 m length, 0.53 mm ID and 40 μm film thickness. GC method conditions developed for $^{13}\delta$ measurement of CO_2 are given in Table 1.

Table 1. GC Parameters

Injector:	Splitless mode
Injection volume:	800 μL
Injection temp.:	200 °C
Carrier gas:	Helium, constant flow 10 ml/min

Activities in 1.2.4

Task 1.2.4 : 4 reference standard mixtures of CO_2 with different isotopic compositions

Delivery Date : January 2016

Participants : NPL

- These mixtures have now been made at NPL:

CO_2 source	δ value	Amount fraction [μmol/mol]				
Underground source	-4.5		380*			
NPL blend	-8.5	360	380*	400	420	440
Industrial source	-33		380*			
Combustion source	-45		380*			
* Indicates mixtures to be measured at TUBITAK in D1.2.5						

- They will be sent to TUBITAK UME in March 2016.

Future Activities

Task 1.2.5 : Mixtures in D1.2.4 quantified for isotopic composition using IRMS

Delivery Date : May 2016

Participants : TUBITAK

- The mixtures prepared by NPL will be analyzed using IRMS facility at TUBITAK according to the protocol.

Future Activities

Task 1.2.6 : Analytical bias related to CO_2 isotopic composition quantified for CRDS

Delivery Date : November 2016

Participants : NPL

- NPL will compare the mixtures prepared in D1.2.4 using a commercial CRDS to determine the influence of isotopic distribution of CO_2 on the response. This will provide information on possible corrections to CRDS analyser response.