Metrology for biomethane

Measurement techniques and test methods for measuring ammonia content

Lucy Culleton (NPL)

Workshop on conformity assessment of biomethane, Delft, 25th January 2019

Ammonia within EN16723

Parameter	EN 16723-1	EN 16723-2
Silicon concentration	≤ 0.3 to 1 mg/m^3	≤ 0.5 mg/m^3
Hydrogen fraction	See EN 16726	≤ 2 %
Hydrocarbon dew point	See EN 16726	≤ -2 °C
Oxygen fraction	See EN 16726	≤ 1 %
Sulphur concentration	≤ 20 mg/m^3	≤ 5 mg/m^3
Methane number	See EN 16726	≥ 65 (80 for high grade)
Compressor oil content	“de deminis”	“de deminis”
Dust impurities	“de deminis”	≤ 10 mg/L
Amines content	≤ 10 mg/m^3	≤ 10 mg/m^3
Water dew point	See EN 16726	≤ -10 °C
Chloride concentration	“de deminis”	
Fluoride concentration	“de deminis”	
Carbon monoxide fraction	≤ 0.1 %	
Ammonia concentration	≤ 10 mg/m^3	

Green = Capability developed at NPL

Ammonia is corrosive in water and contributes to formation of NO_X

Ammonia work within METROLOGY FOR BIOMETHANE project

NPL National Physical Laboratory

Aim

To develop stable, metrologically traceable and accurate measurement standards and high-accuracy reference methods for ammonia in biomethane

Traceable gas standards

Validated measurement methods

Partners:

NPL National Physical Laboratory

VSL

INNOVHUB STAZIONI SPERIMENTALI PER L'INDUSTRIA

Innovazione e ricerca

RICE Research & Innovation Center for Energy

GRTgaz

VTT

METROLOGY FOR BIOMETHANE

Task 2.1: Improved stability of ammonia measurement standards

Activity number	Activity description
A2.1.1	Identify cylinder types

- 6 passivation types were selected

sampling vessel

Cylinder types
BOC spectraseal
NET
Effectech Performax
Scott Aculife IV
Air products Experis
SilcoTek Sulfinert

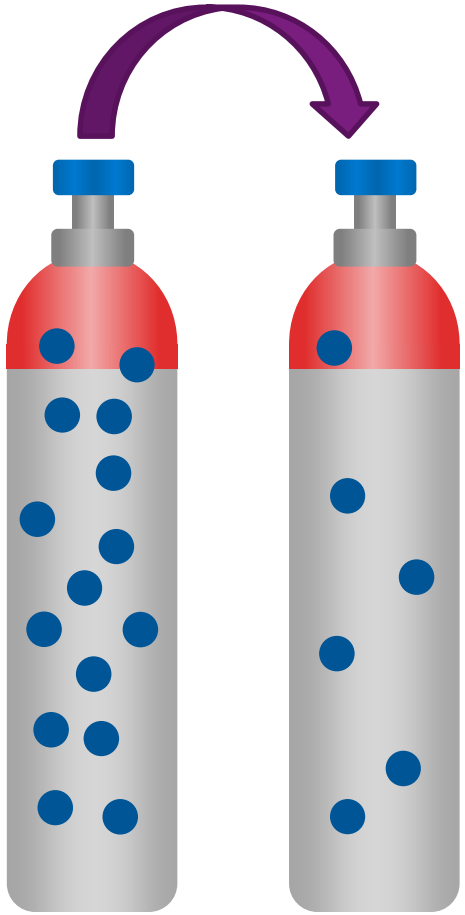
Task 2.1: Improved stability of ammonia measurement standards

Activity number	Activity description
A2.1.2	Prepare gas reference standards

- 7 reference standards were prepared

How ammonia standards are prepared

- **10 mg/m³** only possible via **multi-stage dilution**



METROLOGY FOR BIOMETHANE

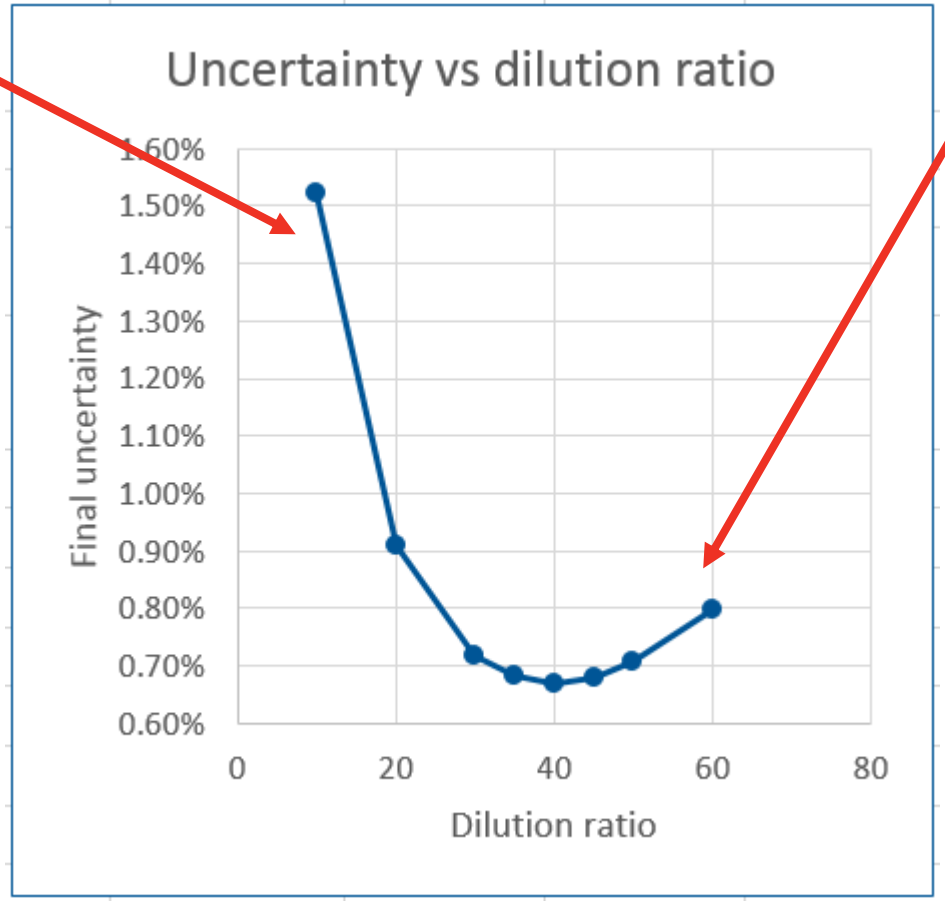
How ammonia standards are prepared

Lower amount fraction grandparent
(Use more to make parent)

Higher amount fraction grandparent
(Use less to make parent)

High uncertainty

Low uncertainty



Low uncertainty

High uncertainty

How ammonia standards are prepared

- Gravimetric preparation

Pure ammonia

Transfer vessel
(loop)

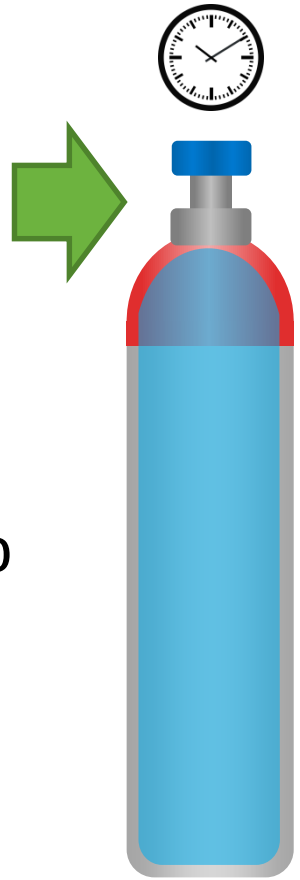
High-accuracy
weighing

Tare vessel

How ammonia standards are prepared

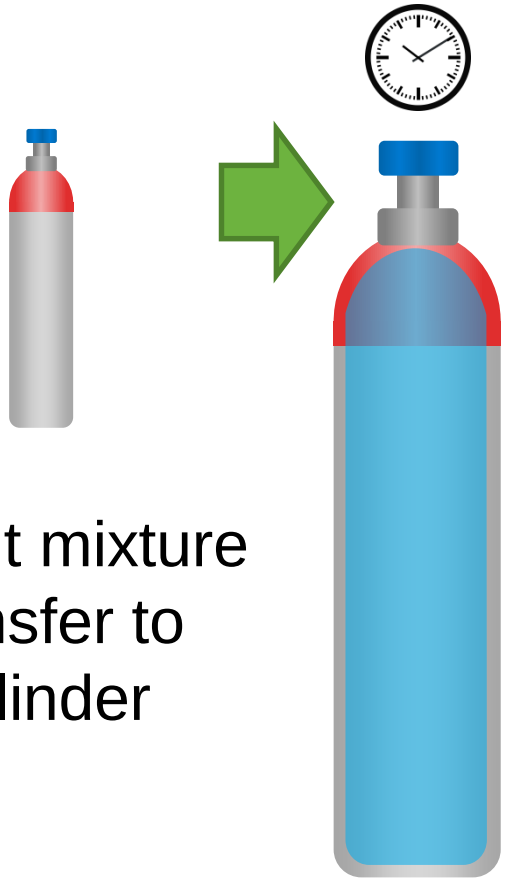
Example of pure NH_3 being transferred to a small vessel

How ammonia standards are prepared



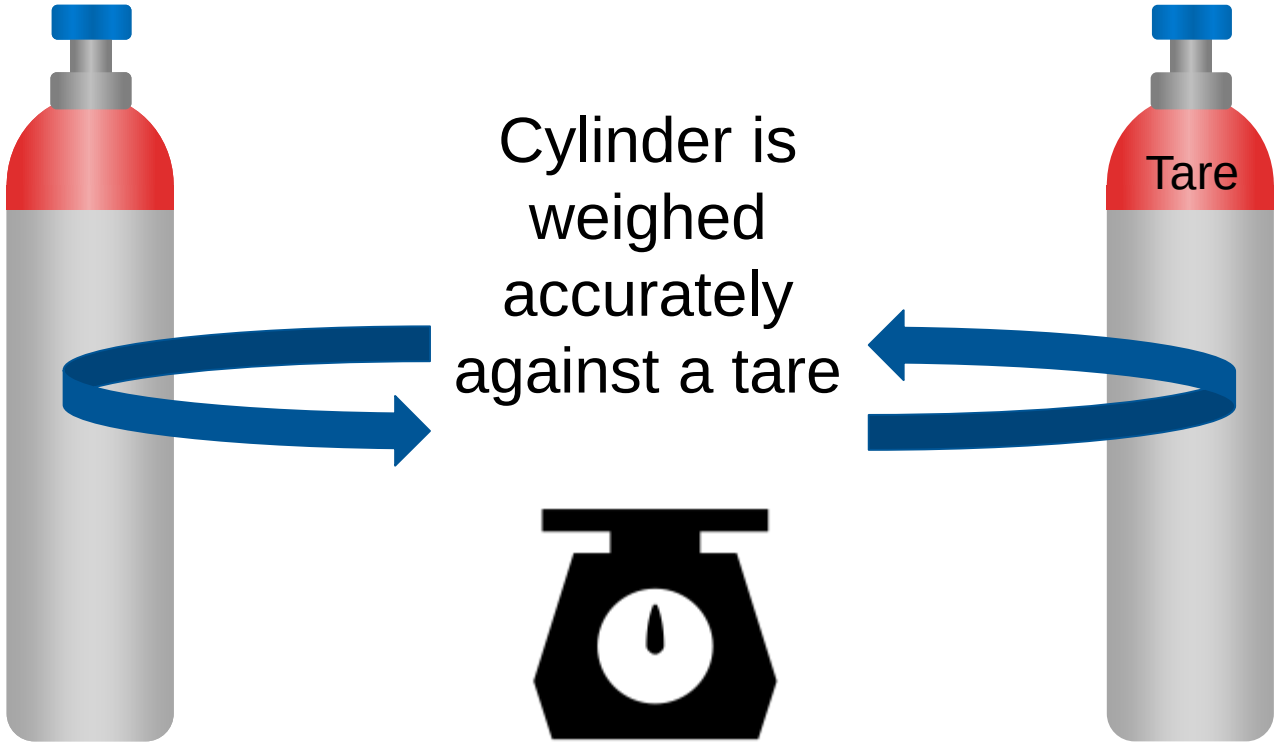
Transfer to cylinder

How ammonia standards are prepared

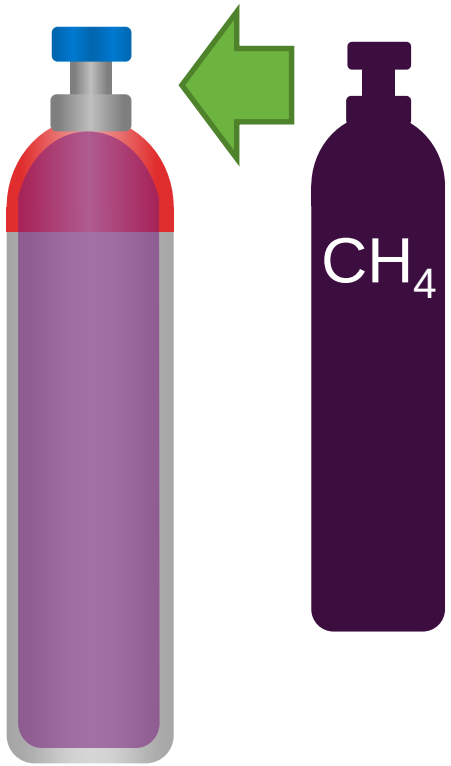


Parent mixture transfer to cylinder

How ammonia standards are prepared

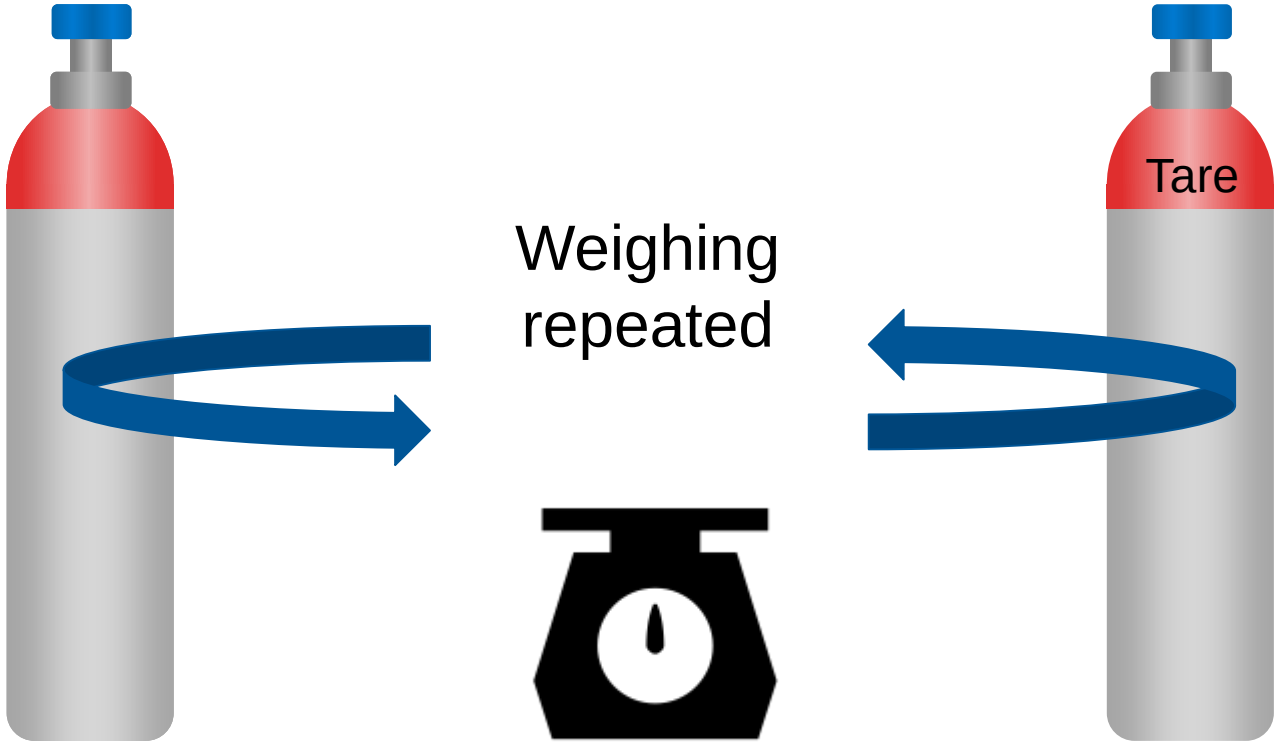


How ammonia standards are prepared



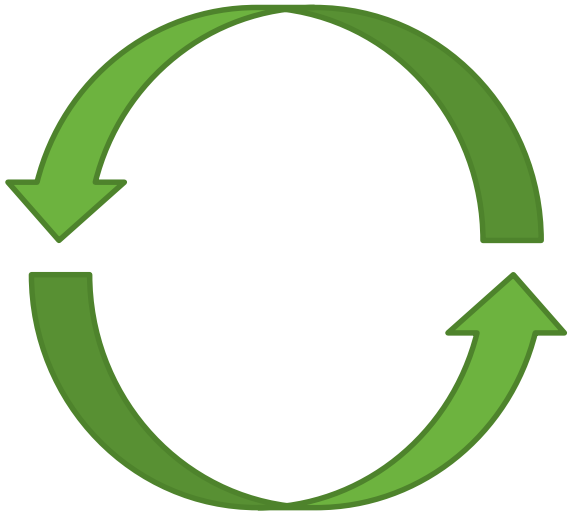
Balance gas is transfered

How ammonia standards are prepared



How ammonia standards are prepared

- Cylinder is **rolled** to homogenise



Preliminary results

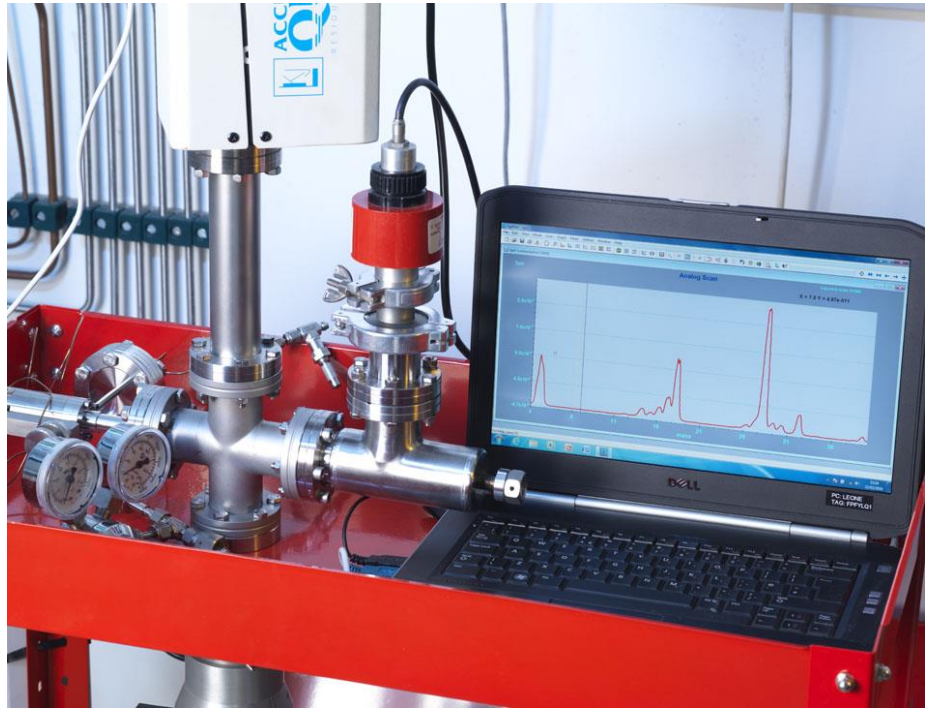
- **Standards initially measured using NDIR sprectometry**

Cylinder types	Cylinder no.	Certified NH_3 concentration against the reference cylinder 2462	% deviation from gravimetric concentration	Analy. U/C (k=2) rel. %
A	D679217	10.2	2.3	1.2
B	D618312	9.3	-6.3	0.8
C	2426	10.1	1.4	1.2
D	L53103038	11.6	15.9	1.1
E	0606	10.0	0.5	1.5
F	APEX1182786	9.8	-2.1	1.6
G	RK7065	10.0	-0.7	2.1

Task 2.1: Improved stability of ammonia measurement standards

Activity number	Activity description
A2.1.3	NPL will quantify ammonia interaction with surfaces using a materials testing rig

- **Ongoing work**



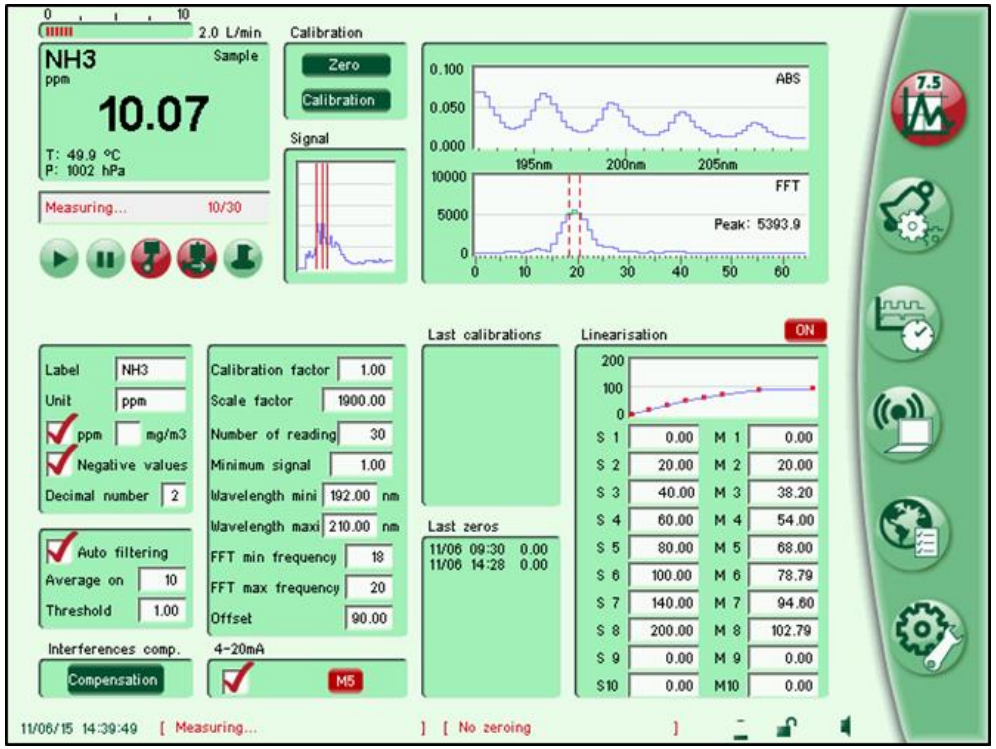
Task 2.1: Improved stability of ammonia measurement standards

Activity number	Activity description
A2.1.4	NPL will generate a **dynamic standard** to compare against static standards

- **Ongoing work**

Task 3.1 - Test method for ammonia

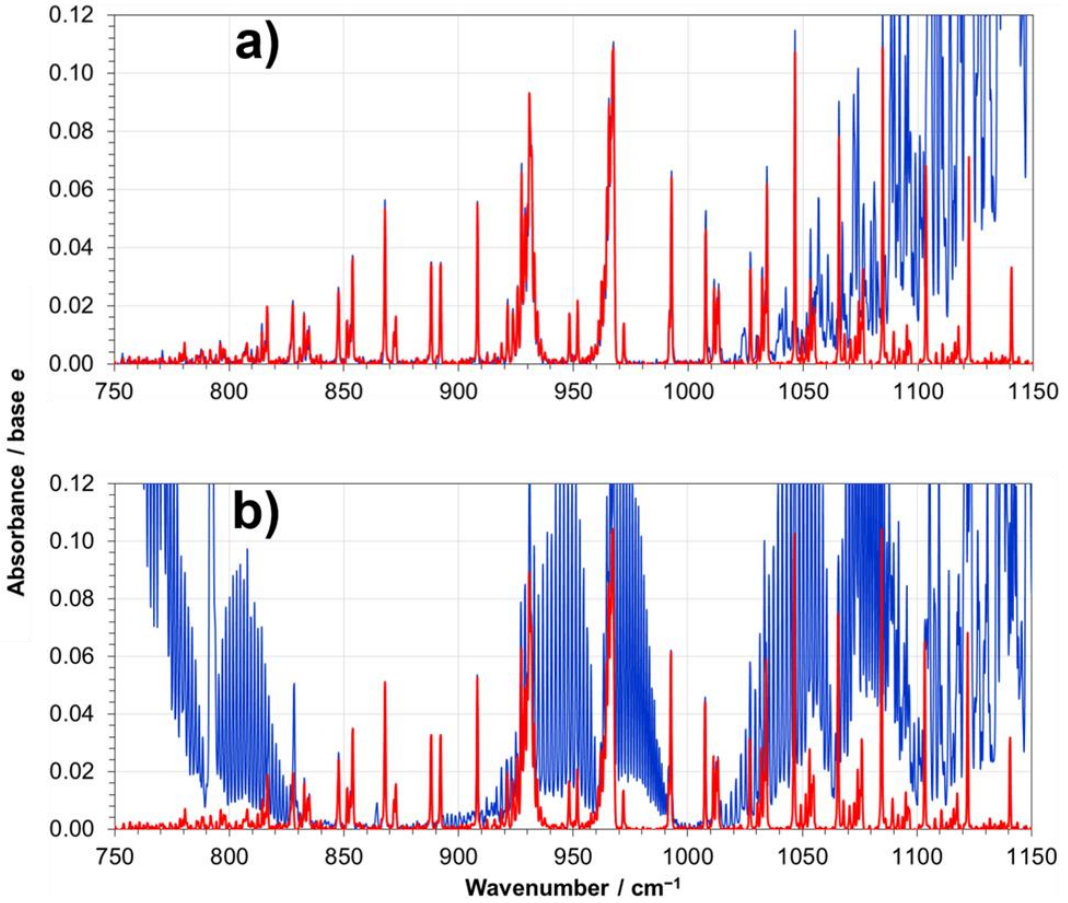
Activity number	Activity description
A3.1.4	NPL will develop and validate an applicative method for the analysis of ammonia in biomethane using UV-VIS detection.



Previous measurement of ammonia at NPL

- Simulated FTIR spectra of 10ppm ammonia mixtures
- Matrix comparison: Biogas, methane and nitrogen

- NH3 in N2 (red) and in CH4 (blue),



- NH3 in N2 (red) and in Biogas (blue)

NPL
National Physical Laboratory

Department for
Business, Energy
& Industrial Strategy

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METROLOGY FOR BIOMETHANE

Workshop on conformity assessment of biomethane organised by the project EURAMET EMPIR 16ENG052 “Metrology for Biomethane” and ISO/TC193/SC1/WG25 “Biomethane”

Measurement technique and test method for measuring total silicone in biogas/biomethane - Method developed at IMBiH

Work done by Katarina Hafner-Vuk and Rialda Kurtić
Presentation prepared by Rialda Kurtić

Workshop on conformity assessement of biomethane
NEN, Vlinderweg 6, Delft, the Netherlands, 22-23 January 2019

CONTENTS

- Description of instrumental technique
- Instrumental method set-up
- Sampling of siloxanes from biogas/biomethane
- Results
- Conclusions

Description of instrumental technique

- Microwave Plasma – Atomic Emission Spectrometer (MP-AES) (Figure1)
- MP AES technique is based on the emission of photons from atoms or ions that have been excited in microwave nitrogen plasma (Figure 2)
- Simultaneous multi-analyte determination.
- Sample type: Liquid
-Sample introduction: peristaltic pump, nebulizer with nebulizer chamber

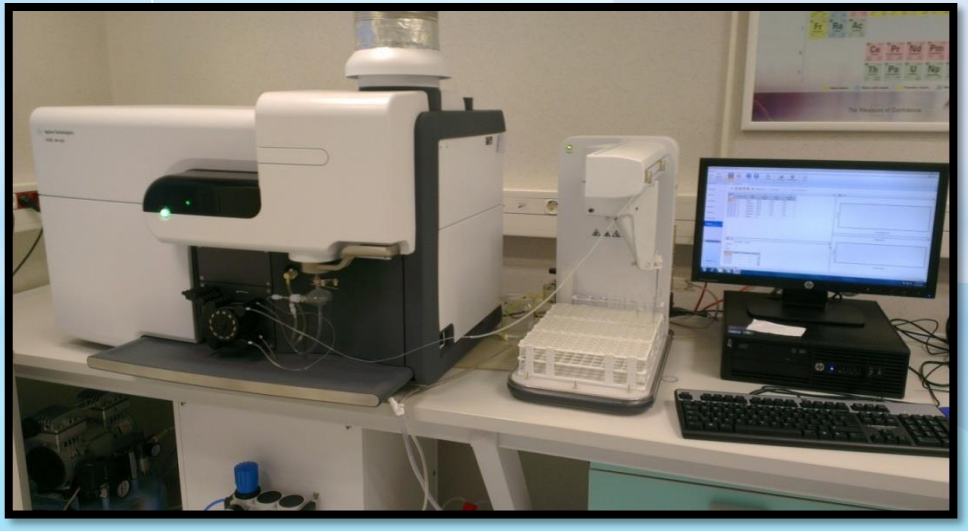


Figure 1. MP AES in Laboratory for Chemistry at IMBIH

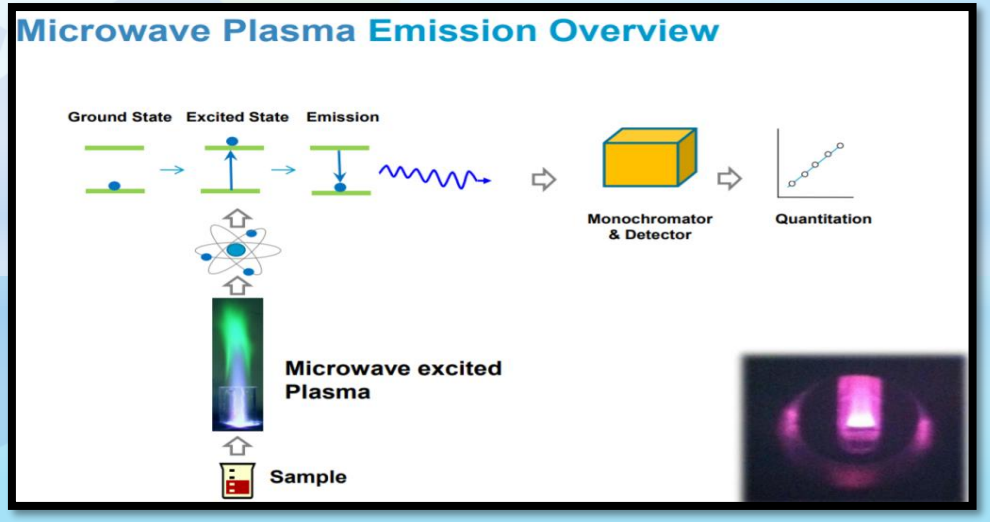
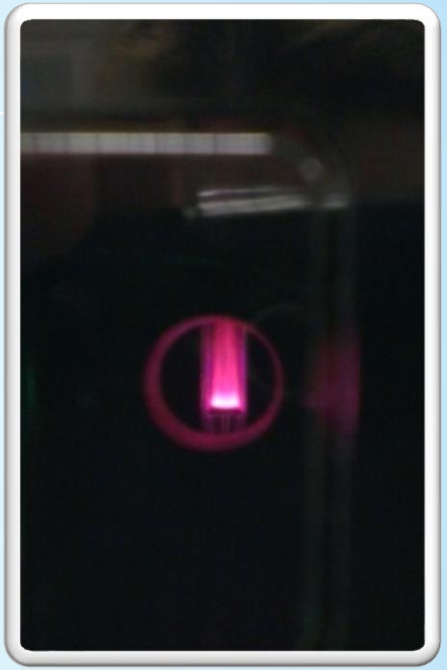


Figure 2. Explains the principle of MP-AES

Description of instrumental technique



Sample introduction: peristaltic pump, nebulizer with nebulizer chamber

Sample path: nebulizer with nebulizer chamber, N_2 plasma, break down into atoms or ions, get excited and in the end emit the photon

Properties of microwave induced N_2 plasma

- inert

- high temperature of the microwave plasma helps to reduce chemical interferences.

Detector covers near UV and visible part of the spectra.

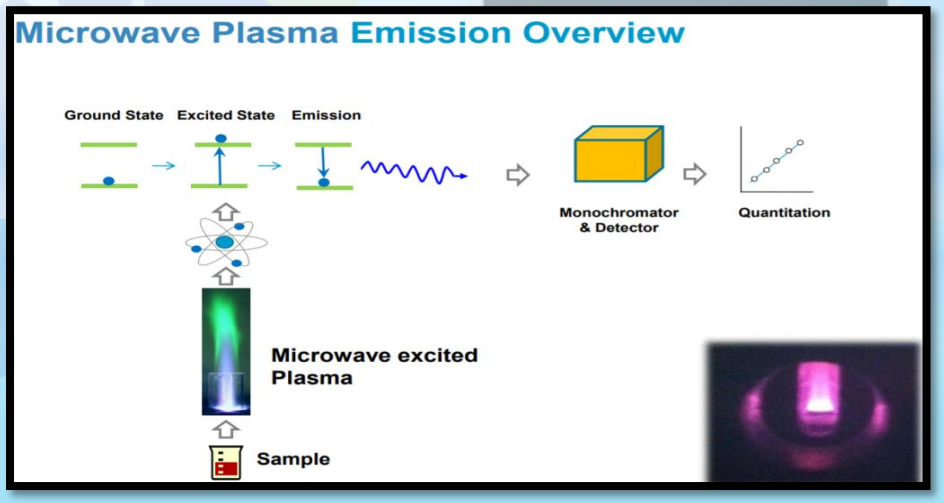


Figure 2. Explains the principle of MP-AES

Description of instrumental technique

Operating parameters of MP-AES	
Instrumentation	**Agilent 4200 Microwave Plasma AES with 4107 Nitrogen Generator**
Plasma conditions	
Plasma Gas	N_2 by using both Air Compressor and N_2 Generator (air compressor feeds the air to the N_2 generator)
Power of Magnetron Output	1 kW
Gas flows	
Plasma Gas Flow-Nitrogen	20 L/min (fixed)
Pre-optics Protection (POP) Gas –Air	25 L/min
Nebulizer gas flow	Nebulizer gas flow is computer controlled using mass fl ow control to provide accurate flow control in the range 0.3–1.0 L/min.
Nebulizer	OneNeb™ inert concentric for HF and high TDS solutions
Spray Chamber	Double-pass glass cyclonic
Solution Uptake	1.4 mL/min (pumped)
Pump Tubing	1.02 mm i.d. PVC
Plasma Torch	Quartz torch
Plasma Viewing	Axial
Data acquisition parameters	
Sample Uptake Delay	30s
Stabilization Time	30s
Read Time	5
No. of Replicates	6
Background Correction	**Auto** or FLIC (Fast Linear Interference Correction)
Optical System	Czerny-Turner monochromator with 600 mm focal length and fixed entrance slit
Optical Resolution	< 0.050 nm (measured as full width at half maximum)
Detector	Back thinned solid state CCD detector (532 x 128 pixels)
Analytes (Wavelengths)	**Si 251,611 nm** and 288,158 nm

Table 1. Operating parameters of MP AES

The emission intensities for different elements studied depend on gas flow, sample flow rate, and microwave power.

The nebulizer gas flow and other operating parameters were optimized for obtaining higher stability of plasma and maximum emission intensity.

Instrumental method set up

MP Expert Software

Elements

Wavelengths were set up with respect to possible interferences on Si. **251,611 nm** (most sensitive line); 288,158 nm

Conditions

Nebulizer pressure and **viewing position** were set each time prior analysis with one of the calibration standard solution. Conditions described in ***Table1.***

Detailes on optimized MWP AES parameters	
Pump speed (rpm)	15
Sample introduction	Autosampler
Replicates	6
Uptake time (s)	30 (fast pump ON)
Rinse time (s)	30 (fast pump ON)
Stabilization time (s)	30
QC active	ON
Element (wavelength, nm)	Si **251,611 nm** and 288,158 nm
Background correction	Auto
Calibration correlation coefficient limit set up	0,95 (20% of error)

Table 2. Operating parameters of MP AES

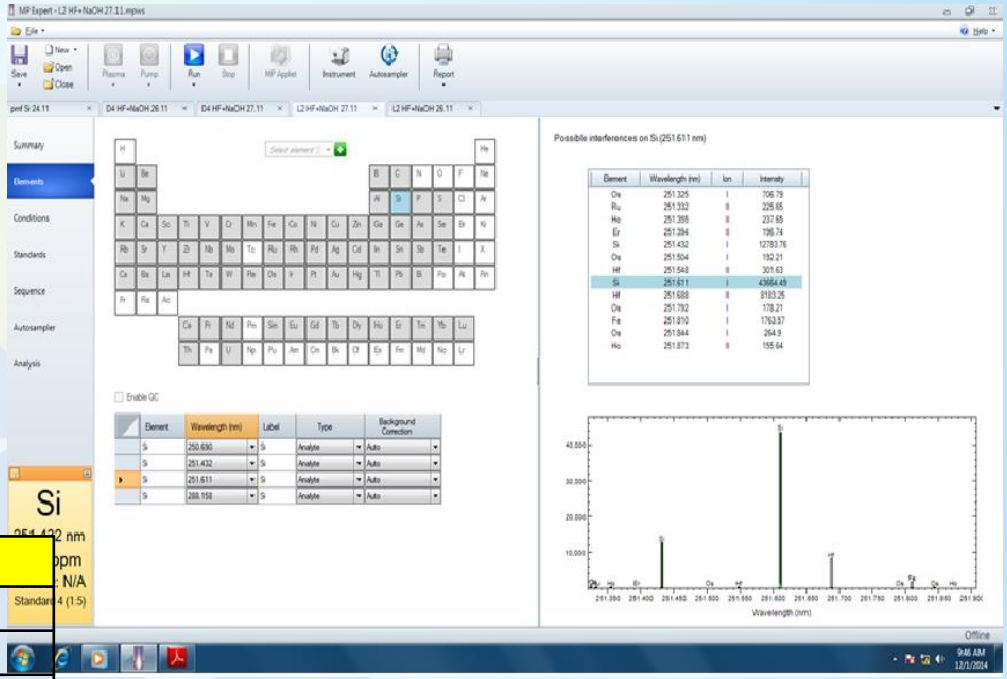


Figure 3 Example of MP Expert Software skreen

Instrumental method set up

Calibration

Calibration curve settings (concentration range) set in such a way to cover the expected concentration of Si from the gas sample.

Calibration standards prepared with reference solution of NH_4HSiF_6(1000 mg/L Si in 2% HNO_3)
Concentration intervals 0,05 – 1 ppm; 1-50 ppm (LOQ at **251,611nm** around 10 ppb).

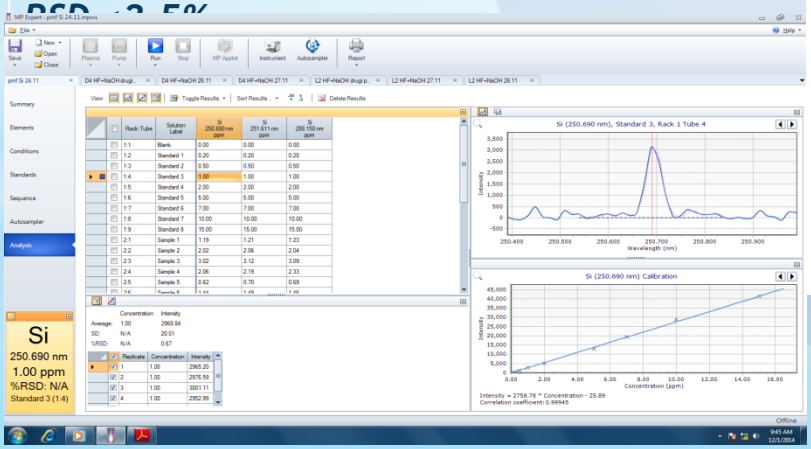
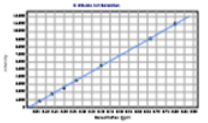


Figure 3 Example of MP Expert Software screen

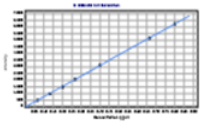
Report Date: Wednesday, July 13, 2016 10:48 AM 15.04.16. DS i uzorkovanje 2 kalibracija (NH4)2SiF6.mpws

Si (251.611 nm)
Intensity = 13879.8848 * Concentration - 92.0139
Correlation coefficient: 0.99986



Standards	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	-0.0253	0.0000	0.0066	N/A
Standard 1	852.8082	0.0666	0.0681	2.25
Standard 2	1747.1017	0.1332	0.1325	0.53
Standard 3	2601.1096	0.1998	0.1940	2.90
Standard 4	3643.1524	0.2664	0.2691	1.01
Standard 5	5552.5562	0.3996	0.4067	1.78
Standard 6	9121.7492	0.6660	0.6638	0.33
Standard 7	11113.3013	0.7992	0.8073	1.01

Si (288.158 nm)
Intensity = 7815.4902 * Concentration - 9.5697
Correlation coefficient: 0.99991



Standards	Intensity	Method Concentration	Calculated Concentration	% Error
Blank	0.0081	0.0000	0.0012	N/A
Standard 1	508.9724	0.0666	0.0663	0.45
Standard 2	1002.0844	0.1332	0.1294	2.85
Standard 3	1517.9810	0.1998	0.1955	2.15
Standard 4	2090.8223	0.2664	0.2687	0.86
Standard 5	3169.5908	0.3996	0.4068	1.80
Standard 6	5171.7591	0.6660	0.6630	0.45
Standard 7	6248.0388	0.7992	0.8007	0.19

Figure 5. *Examples of calibration curves (*emission lines: 251,611 nm; 288,158 nm) obtained in proces of method validation

Sampling of siloxanes from biogas/biomethane – method of choice

Sample type for MWP AES: Liquid (an anorganic solvent, for organic solvent additional accessories required)

Sampling in $HNO_{3(conc.)}$ and other acidic media did not show good results with MWP AES technique (TDS>3%, required dilution of concentrated acidic media)

The form of the silicon is highly dependent on the pH of the solution during the derivatization process!

Analyte/ Media	NaOH 0,5M + HF 48% (HF in excess, pH<2)	NaOH 0,5M + HF 48% - HF in excess pH=4	NaOH 0,5M + HF 48% - NaOH in excess	NaOH 0,5M + HF 48% + NaF - HF in excess pH=4
L2	Soluble + Derivatization + Stable + (2 weeks in PP) Homogenous +	Soluble + Derivatization +/- Stable +/- Homogenous +/-	Soluble + Derivatization - Stable - Homogenous -	Soluble + Derivatization +/- Stable +/- Homogenous +/-
D4	Soluble + Derivatization + Stable + (2 weeks in PP) Homogenous +	Soluble + Derivatization +/- Stable - (2 weeks in PP) Homogenous -	Soluble + Derivatization - Stable - Homogenous -	Soluble + Derivatization +/- Stable - Homogenous +

Table 3. Overview of L2&D4 behaviour in selected media

Sampling of siloxanes from biogas/biomethane – method of choice

Sampling method

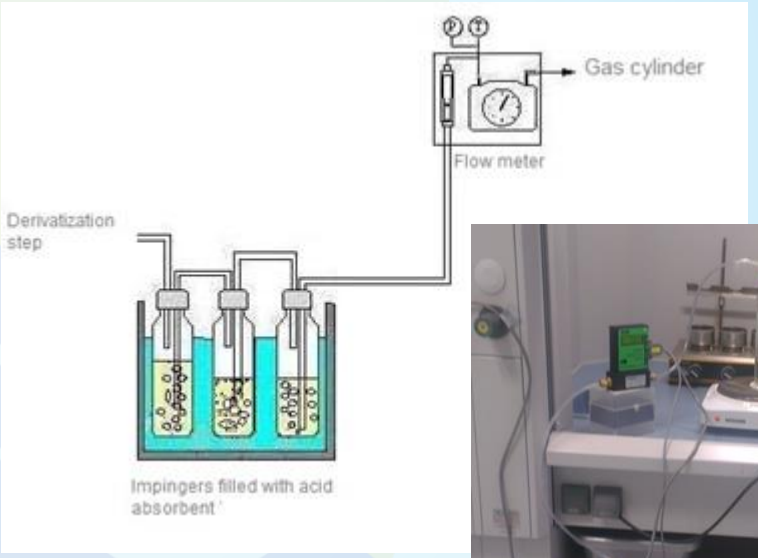
Biogas/biomethane sample passed through absorbing liquid ($HNO_{3\ CONC.}$) heated to around 60ºC.

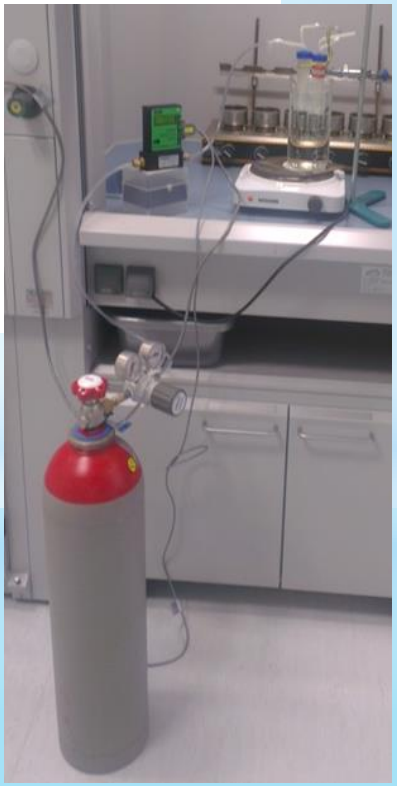
Sampling flow was kept constant at approximately 10 mL/min and the total volume was read from the flow meter after the sampling was finalized.

$HNO_{3conc.}$ from gas impingers was quantitatively transferred to a plastic container and weighed.

Further treatment with concentrated NaOH and HF + dilution with water (Table 3).

The sample was weighted and expected concentration calculated (assuming 100% efficiency of sampling and derivatization proces)



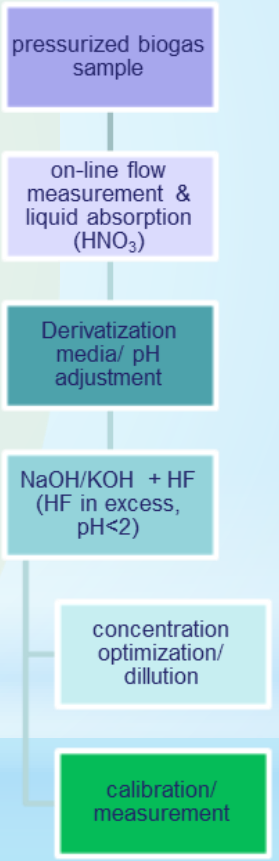


Sampling of siloxanes from biogas/biomethane – method of choice

Two gaseous referent mixtures with different concentration of the siloxanes were used for sampling of a siloxane with the purpose of final determination of silicone.
1. One with low Si content containing the following components and concentrations:

L2 – 0.24135 ppm (grav.)
L3 – 0.03527 ppm (grav.)
D4 – 0.87933 ppm (grav.)
D5 – 0.05614 ppm (grav.)

2. Second one as D5 parent mixture with nominal concentration of D5 6 µmol/mol
This mixture corresponds with the overall silicon content of 5 mg/m3.



Flowchart for preparation gaseus sample for MPW AES analysis

RESULTS

Sample/Parameter	Sample 1 (low conc.)	Sample 2 (low conc.)	Sample 3 (low conc.)	Sample 4 (low conc.)	Sample 1 (D5 mixture)	Sample 2 (D5 mixture)
Volume collected (at atmospheric pressure)	48,2 dm^3	55,10 dm^3	48,5 dm^3	38,36 dm^3	2,70 dm^3	2,28 dm^3
Mass of liquid sample	120,46 g	128,92 g	145,53 g	142,3 g	178,9 g	163,0 g
Dilution factor	100 and 50	100 and 50	100 and 50	100 and 50	1000	1000
Calculated Si conc. assuming 100% efficiency	2,00 ppm	2,14 ppm	1,67 ppm	1,35 ppm	364 ppm	394 ppm
Read Si concentration	1,72 ppm	1,74 ppm	1,18 ppm	1,19 ppm	294,2 ppm	256,4
Efficiency	86%	81%	71%	88%	81%	65%

In order to obtain sufficient volume of absorbed gas at low flow ca. 10 mL/min, the sampling time was split in two to three days in order to collect /absorb around 40/50 L of gas.

The final concentration was calculated using available information on first mixture concentration in the gas mixture and the volume of sampled gas.

D5 mixture was sampled with lower volumes of gas considering high concentration.

Conclusions

- Concentrated acidic media used for the collection of silicon present in biogas with derivatization process provides great capacity and robustness towards other components of biogas, enabling relatively smooth operation with raw biogas.

- The method is suitable for the determination of the lower silicon content providing because of the possibility of prolonged sampling pre-concentration for the following derivatization step.

- It is important to note that used instrumentation is not too expensive and that ambient air nitrogen is used as a fuel for the plasma

- Further work on the stated method is required.

Thank you for your attention!

16ENG05 Metrology for Biomethane

Workshop on Conformity Assessment of Biomethane

Measurement techniques & test methods for measuring total silicon & siloxane content

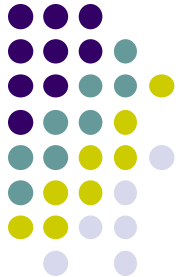
Tim Robinson

Tim_Robinson@wavertonanalytics.com

Overview

- Review of main objectives of Task 3.1: Test Method for total silicon and siloxanes:
  - Practical, environmental and commercial considerations for further discussion
- Overview of prototype specification
- Why GC-FTIR?
- Sample collection & thermal desorption tubes (TDTs)
- Reference calibration library
- Data review: Liquid standard
- Some advantages of TDT-GC-FTIR
- Next steps

Main objectives of Task 3.1



A3.1.5:

- To develop and validate a method for the analysis of speciated siloxanes in biomethane using TDT-GC-FTIR spectroscopy

A3.1.6:

- Analysis of data from three different (analytical) methods to select the standardised test method(s) for the contents of total silicon and siloxanes in biomethane

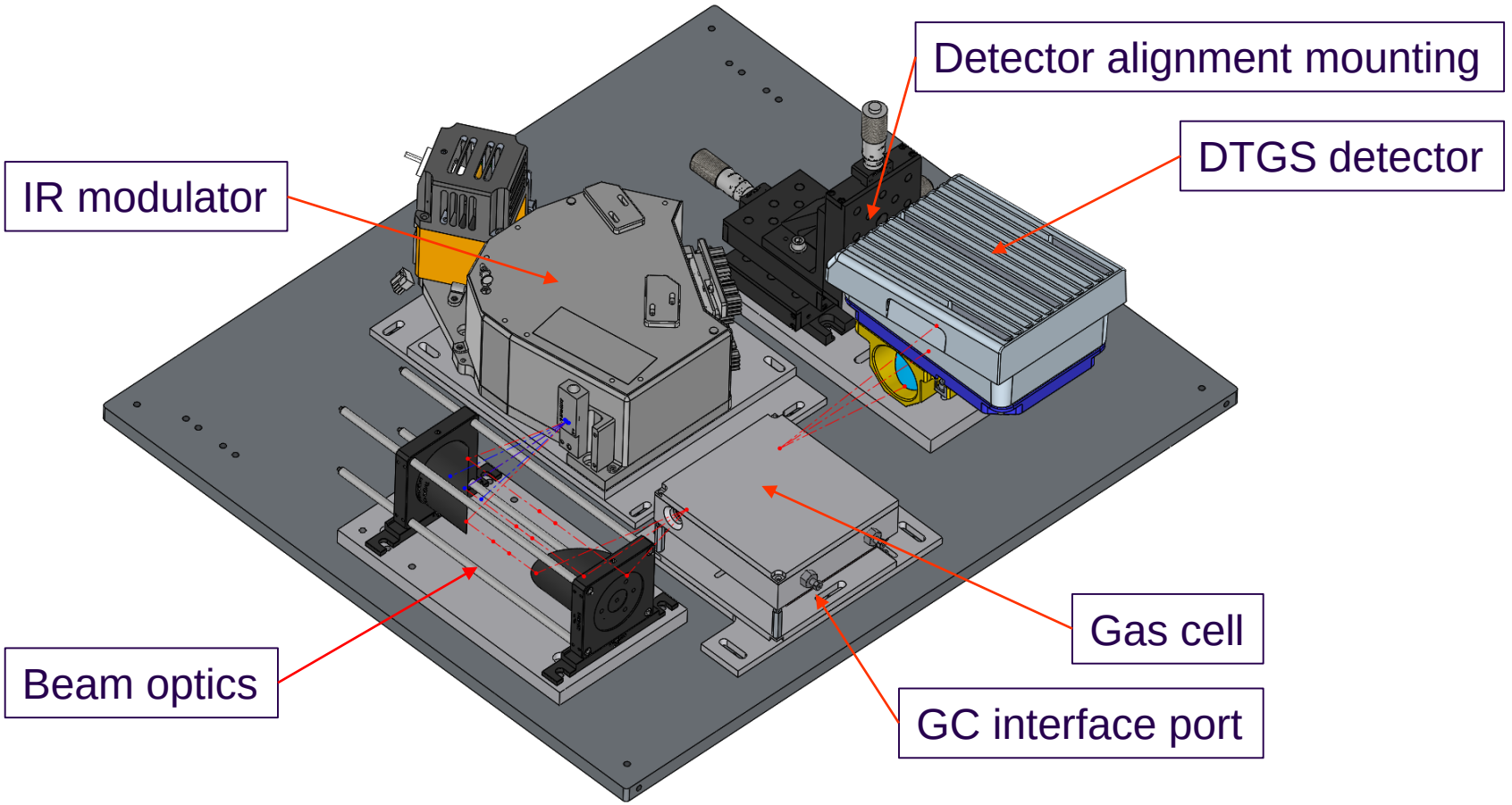
A3.1.7:

- Using input from activities in Task 3.1, write a NWIP for (1) a proposal for a new ISO standard (2) draft text for such an ISO standard for consideration in ISO/TC193/SC1

Parallel considerations:

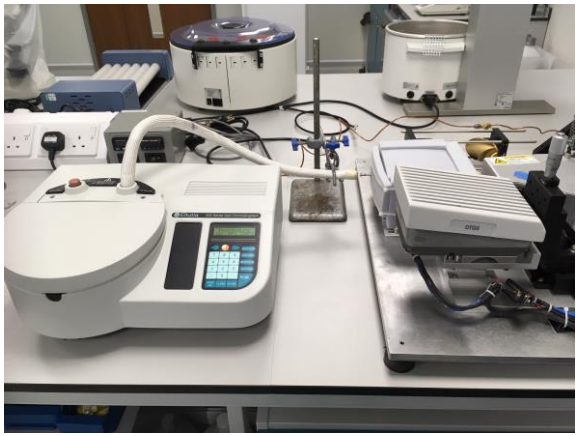
- In-line monitoring or off-line lab-based analysis of samples
- Control and data acquisition requirements / standards
- ATEX certified equipment
- Price versus uptake by industry

Overview of FTIR prototype

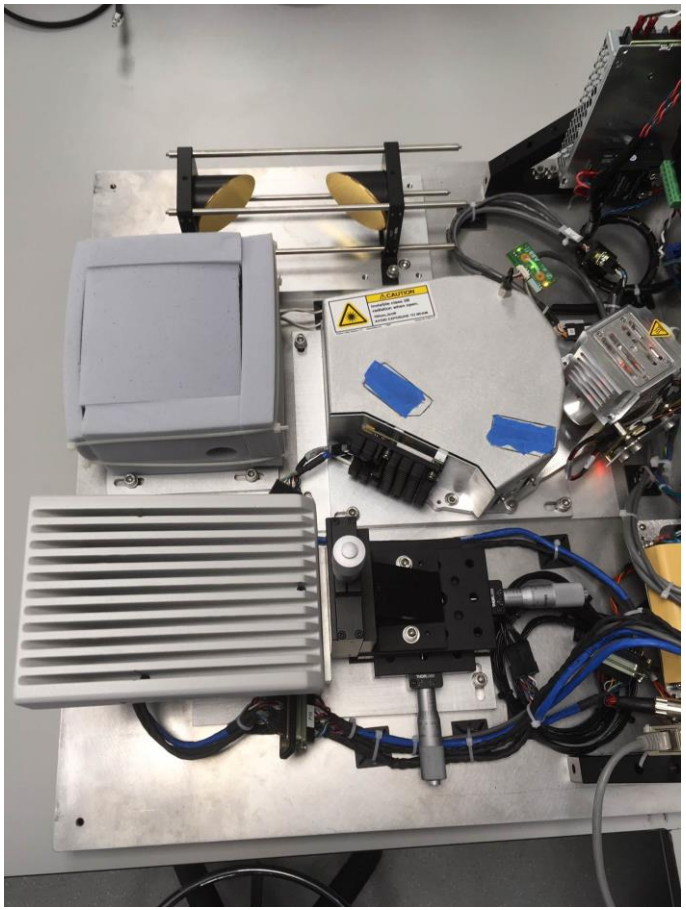


Overview of FTIR prototype

- Spectral range: 500-5000 cm^{-1}
- Resolution: 4 cm^{-1}
- Gas cell: light-pipe type
  - Low volume gas cell for use with GC
- Detector: DTGS type
  - Effective range 400-5000 cm^{-1} – covers siloxane quant region down to 600 cm^{-1}



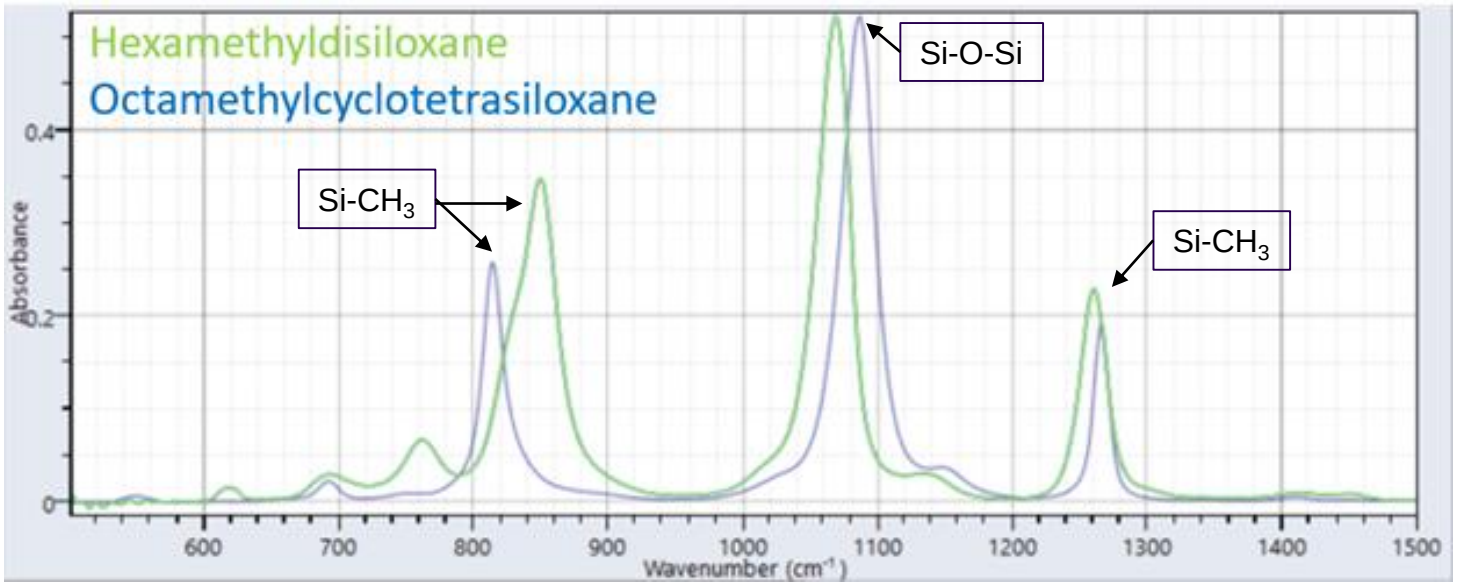
Ellutia 200-series GC Interfaced to FTIR prototype



FTIR “bread-board” prototype

Why GC-FTIR?

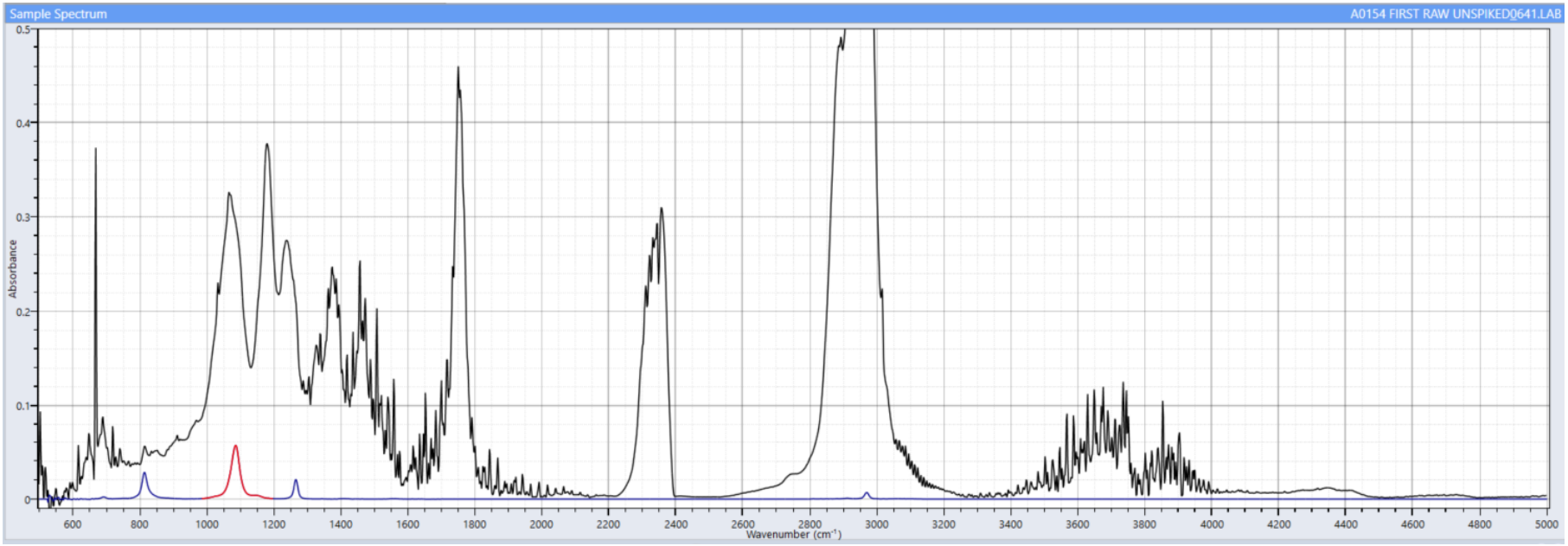
- IR fingerprint region for siloxanes: 600-1400 cm^{-1}
- CO_2 plus many other oxygen containing compounds (alcohols, ketones, aldehydes & esters) also absorb in this region – many present in biogas
- CO_2 not captured by thermal desorption tubes however many other interfering compounds are…



Quant region of IR spectrum for siloxanes

Why GC-FTIR?

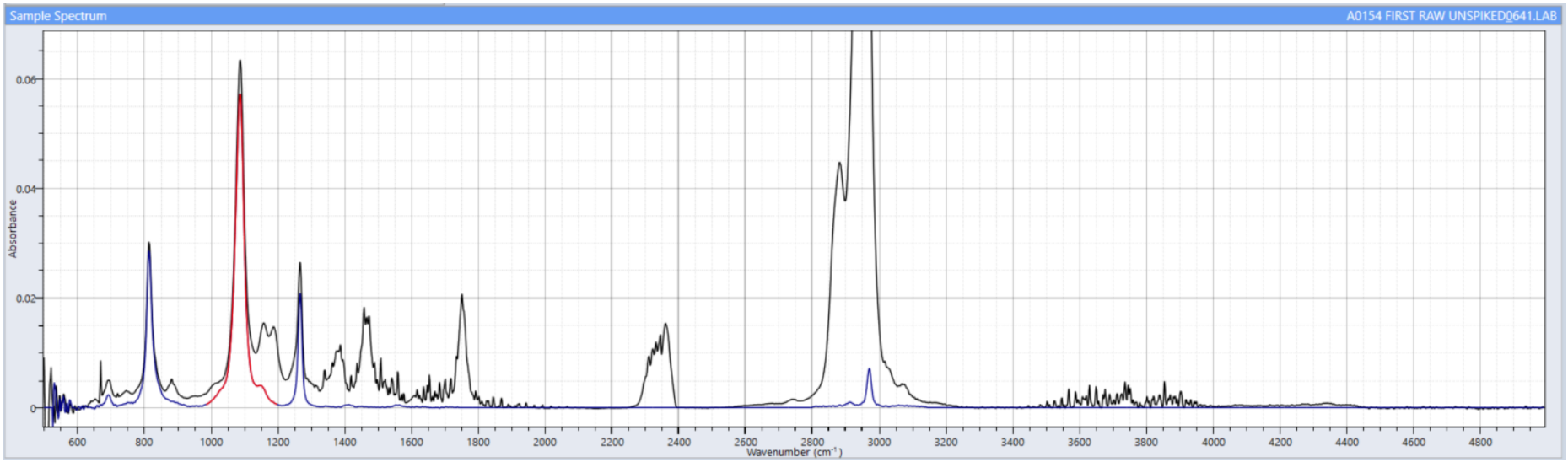
- IR spectrum of raw landfill gas compounds collected on a TDT
- Reference spectrum for octamethylcyclotetrasiloxane (D4) overlaid and scaled to quantified amount present
- Red band primary quant region blue band secondary quant region
- Illustrates analytical challenge associated with interferents



Raw landfill gas IR spectrum

Why GC-FTIR?

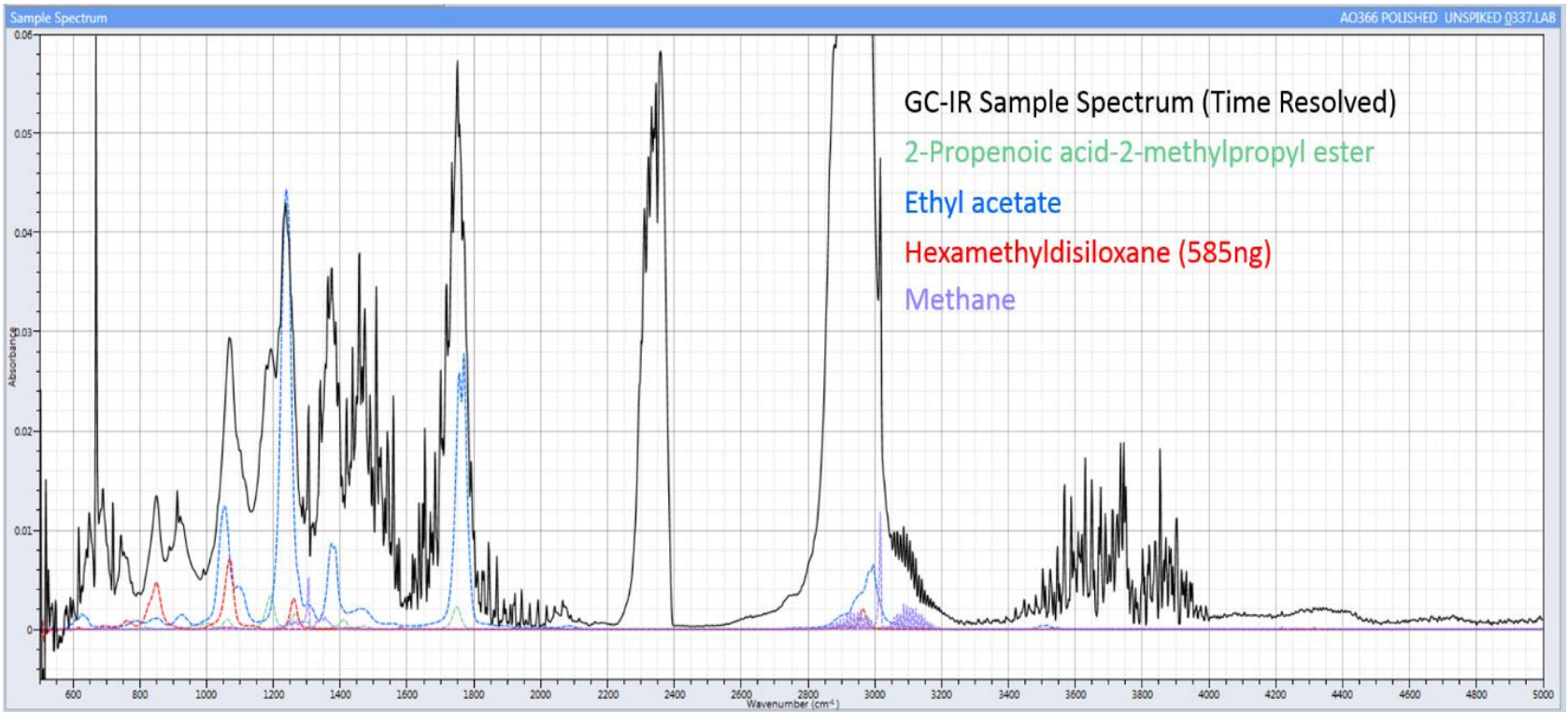
- Same TDT sample however spectrum associated with point at which octamethylcyclotetrasiloxane (D4) comes off the GC column
- Same, scaled reference spectrum overlaid
- Interferents would present analytical challenge for direct FTIR or NDIR measurements, especially when attempting to achieve target detection limits



D4 eluting from GC column

Why GC-FTIR?

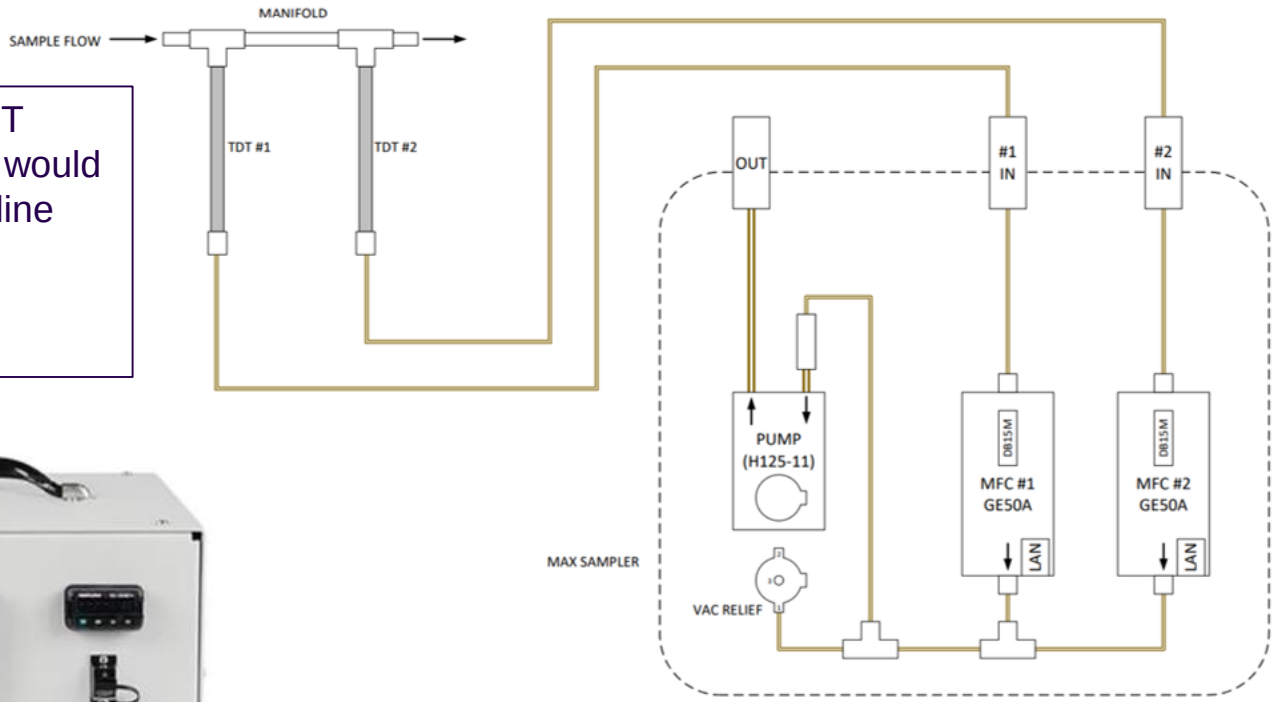
- GC performance not critical to analytical performance – main purpose is to separate majority of critical interferents with time
- Using Restek MXT-624 (30m X 0.53mm X 3.0µm) column
- Algorithm used for quantification of coeluting compounds



Hexamethyldisiloxane (L2) measured in the presence of two coeluting esters

TDT sample collection apparatus

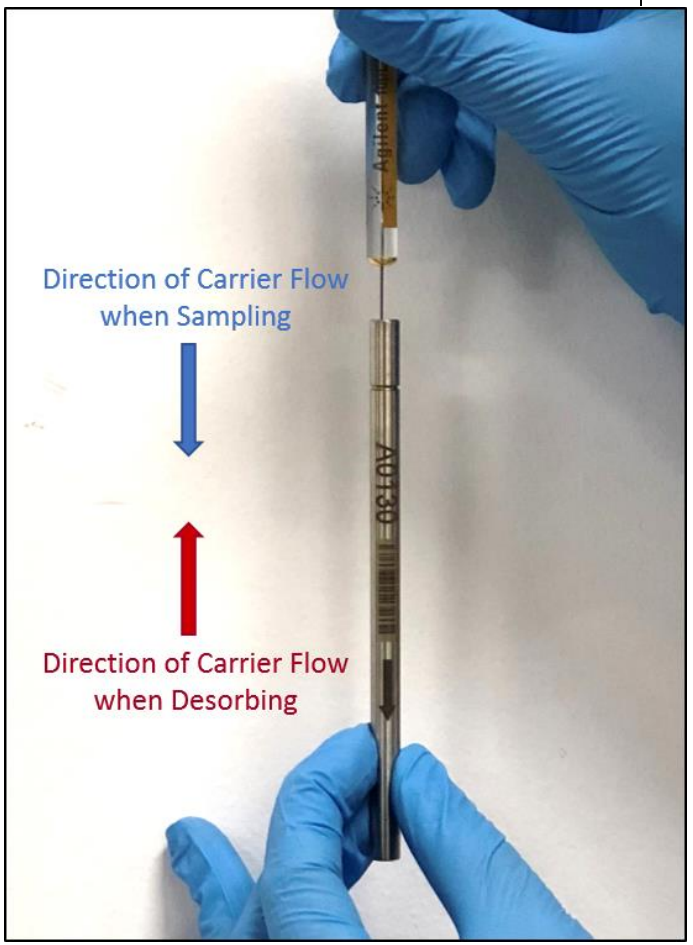
- Sample collection, TDT desorption & analysis would be automated with in-line system
- Second TDT used for “spiking”



Schematic of TDT sampler flow path

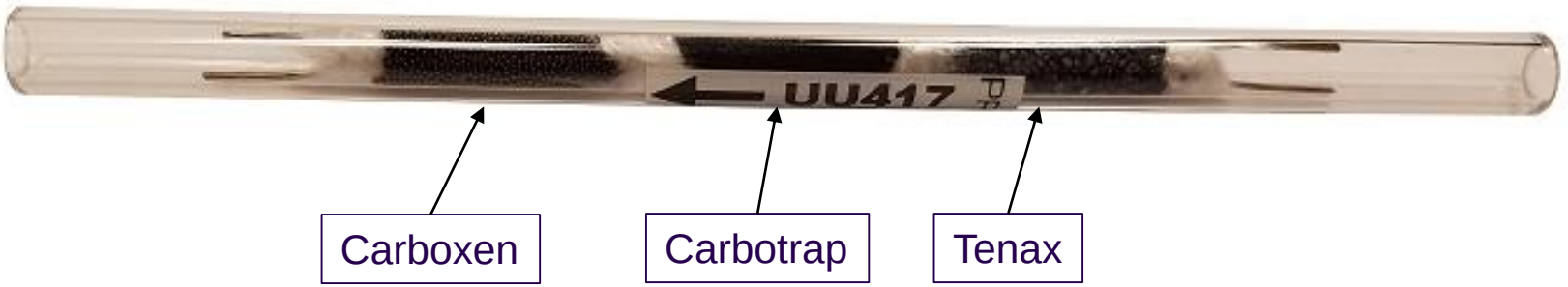
Thermal desorption tubes (TDTs)

- TDT spiking:
  - Determines trapping efficiency for each siloxane
  - Spiked quantity ideally similar to that collected on tube during sampling
- Detection limits:
  - On tube DL of ˜50 ng for each component siloxane
  - Sampling at 100 ml/min for 5 minutes (500 ml of biomethane) → DL of 100 µg/m^3 for each siloxane, or 37 µg Si/m^3 (assuming ˜37% Si content)
  - Target is 0.3 mgSi /m^3 (300 µgSi /m^3) for grid inject 0.1 mgSi /m^3 (100 µgSi /m^3) for vehicle fuel



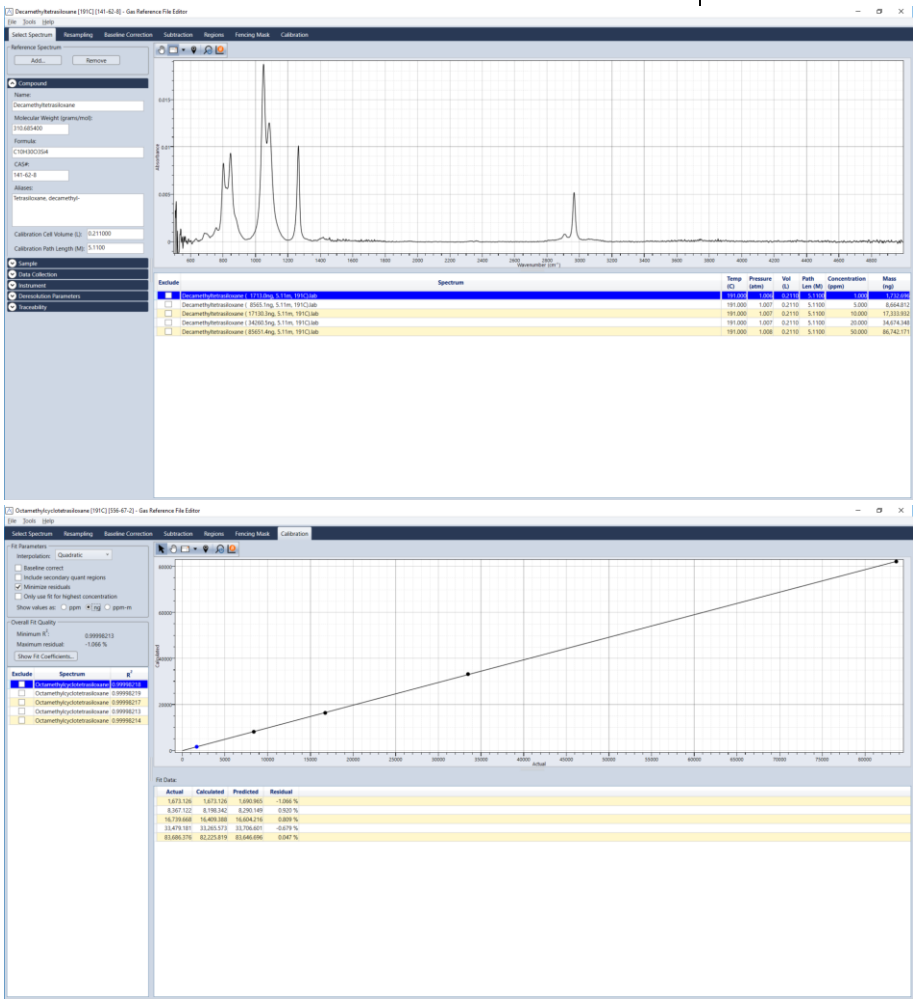
Thermal desorption tubes (TDTs)

- Three-phase media:
  - Texax
  - Carbotrap
  - Carboxen
  - Arranged with increasing sorbent strength
  - Good for general purpose VOC sampling
  - Trapping efficiency for siloxanes >90%



Reference calibration library

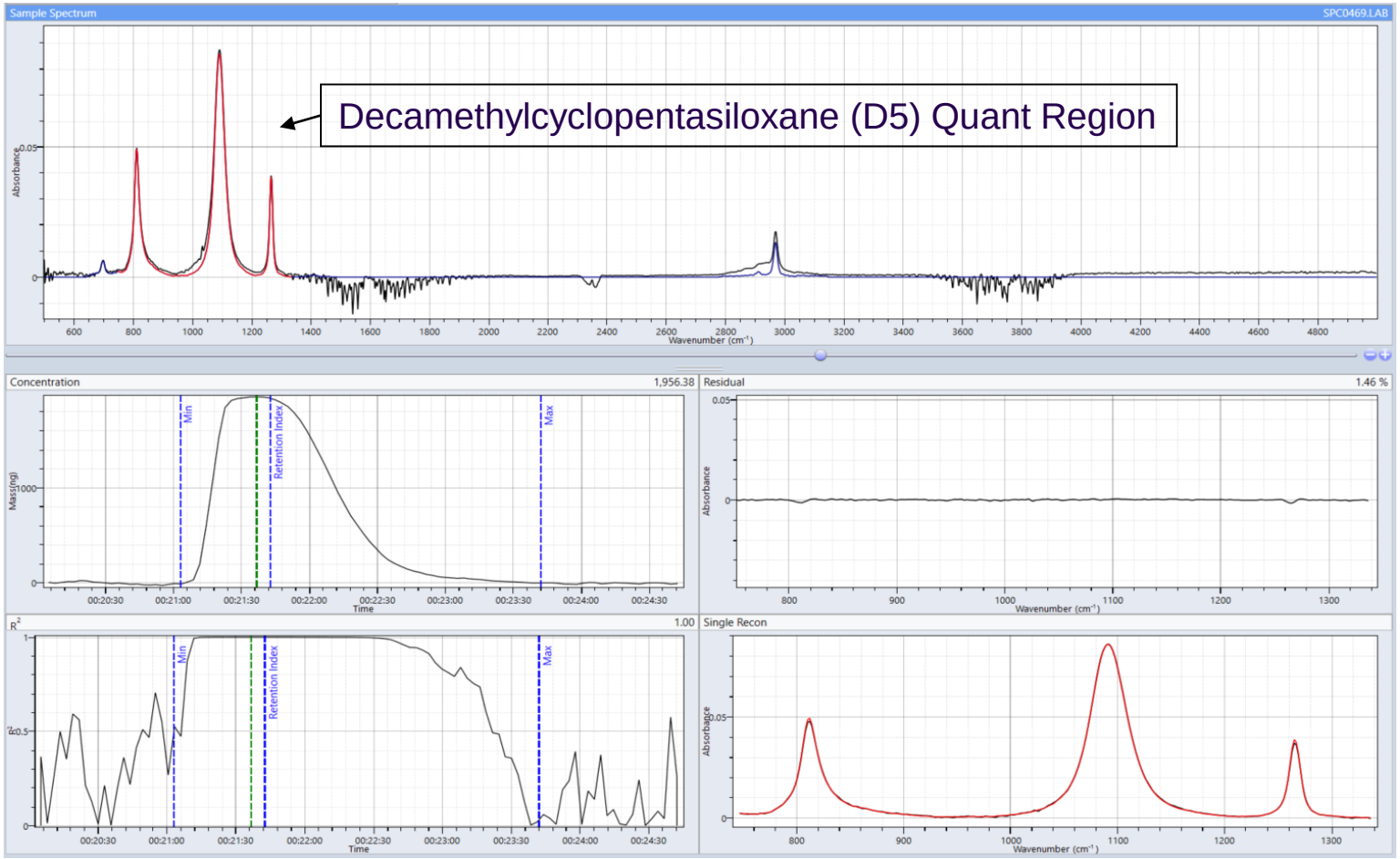
- Reference calibration spectra produced for each siloxane by injecting pure compound into gas cell in a flow of N_2 to dilute
  - 5 points of component dilution
  - Broad, linear range: 0 – 85,000 ng
  - Traceable: equipment calibration and materials certificates of analysis linked to reference:
    - MFCs
    - Syringe & syringe pump
    - Ethylene Calibration Transfer Standard & reference calibration records
    - Purity certificate for siloxane
    - Calibration uncertainty calculations
- 240 quantitative library spectra & 5500 compound identification spectra



Decamethyltetrasiloxane (L4) ref. spectrum

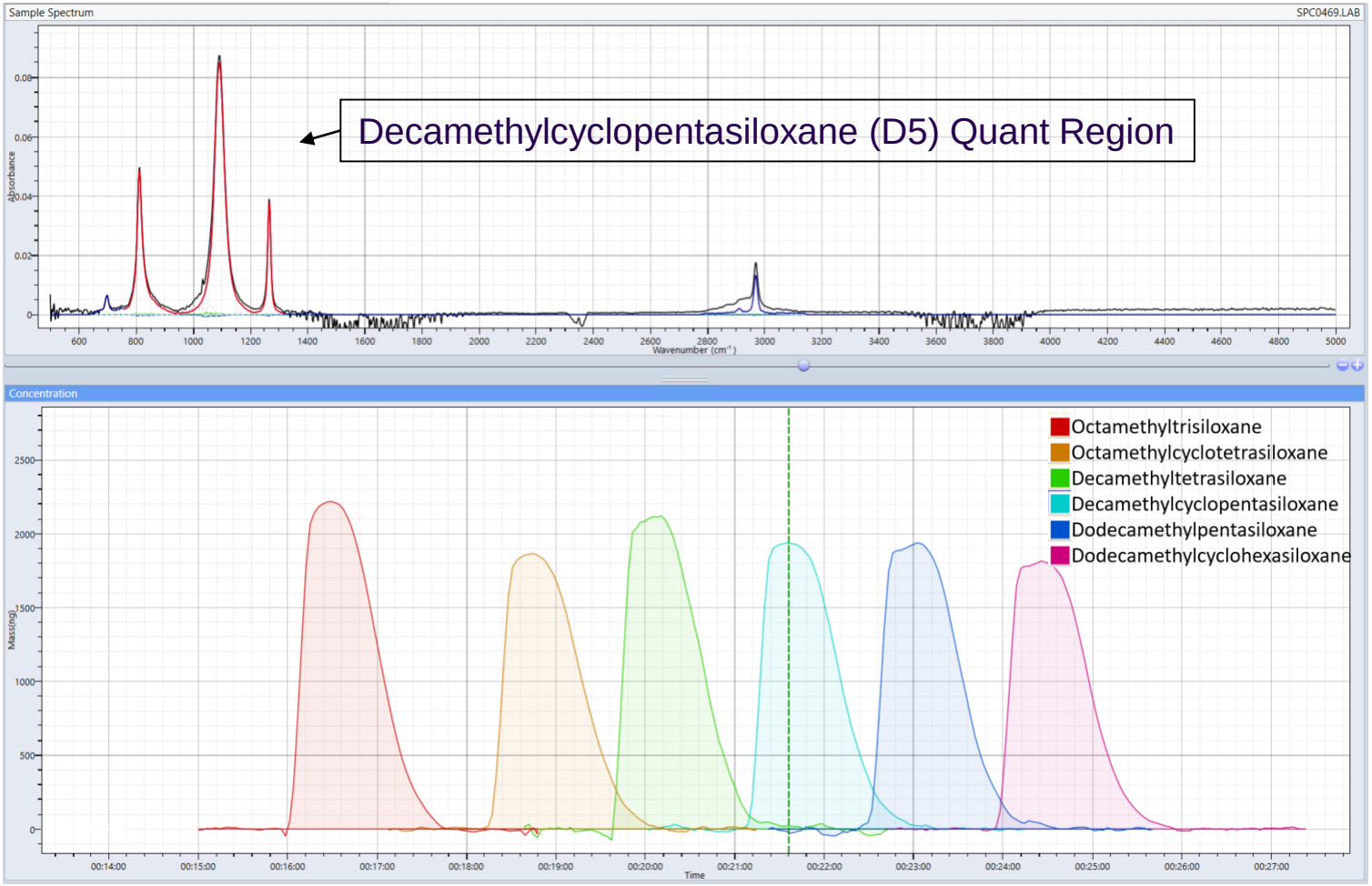
Test data – liquid siloxane standard

- Liquid injection of 1,000 ng/µl siloxane standard from Absolute Standards
- Decamethylcyclopentasiloxane (D5) eluting from column



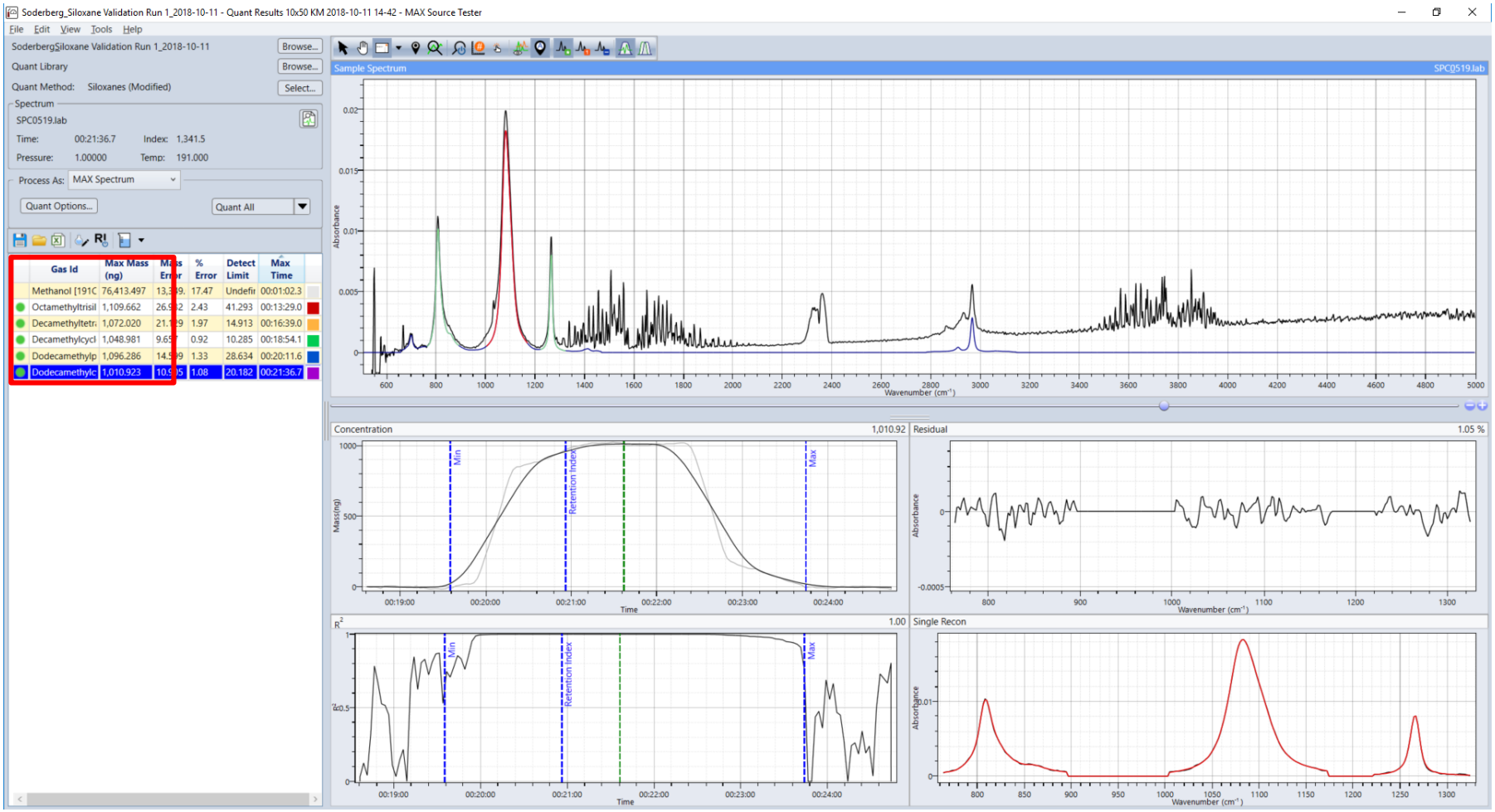
Test data – liquid siloxane standard

- Same liquid standard showing GC separation of all 6 siloxanes



Test data – liquid siloxane standard

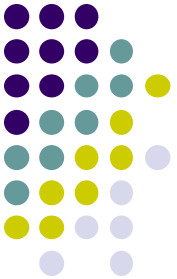
- Quantification of 6 siloxanes at 1000 ng after injecting 1 ul of 1000 ng/ul standard



Some advantages of GC-FTIR

- No vacuum or associated high vacuum pumps required
- Resilient to contamination from components in the sample (ref: ion source contamination with MS-based systems)
- Transportable
- Simple, low cost service requirements (N_2 only, no He or H_2 required)
- Minimal calibration required – uses internal reference spectra
- TDT sampling offers flexibility for for inline and offline (lab) analysis

Next steps



A3.1.5:

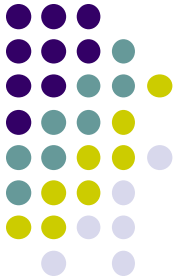
- To develop and validate a method for the analysis of speciated siloxanes in biomethane using TDT-GC-FTIR spectroscopy:
  - Dec-17 – Jul-19: Prototype development using Absolute Standards ref. mixture
  - Oct-18 – Mar-19: Finish first phase of testing with NPL siloxanes standard
  - Jun-19 – Dec-19: Optimise and produce data sets for comparison in A3.1.6

A3.1.6:

- Analysis of data from three different (analytical) methods to select the standardised test method(s) for the contents of total silicon and siloxanes in biomethane:
  - Jan-20 – Feb-20: Comparison of data collected from three methods

A3.1.7:

- Using input from activities in Task 3.1, write a NWIP for (1) a proposal for a new ISO standard (2) draft text for such an ISO standard for consideration in ISO/TC193/SC1:
  - Mar-20 – Apr-20: ISO standard



Thank you!

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