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Analysis of natural gas – Biomethane – Determination of amines content

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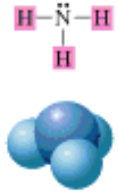
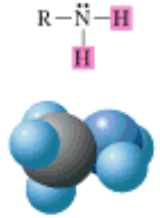
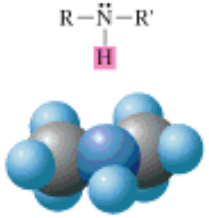
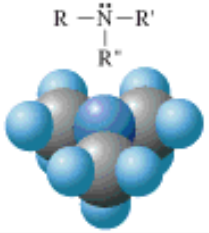
Introduction/context

The alkanolamines are used for removing sulphur-containing components and carbon dioxide in the process of biogas upgrading into biomethane. Due to this reason, some trace level of these components may be present in biomethane.

AMMONIA	PRIMARY AMINE	SECONDARY AMINE	TERTIARY AMINE
			
NH_3	CH_3-NH_2	$CH_3-NH-CH_3$	$CH_3-N(CH_3)-CH_3$

According to the EN16723 specifications, the limit value for amines is maximum = 10mg/m^3.

Why it is needed?

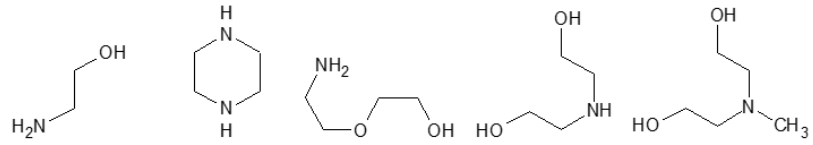
- No measurement standard available, lack of metrological traceability.

- Lack of standardized analytical methods dedicated to the monitoring of amines in biomethane.

Development of measurement standards

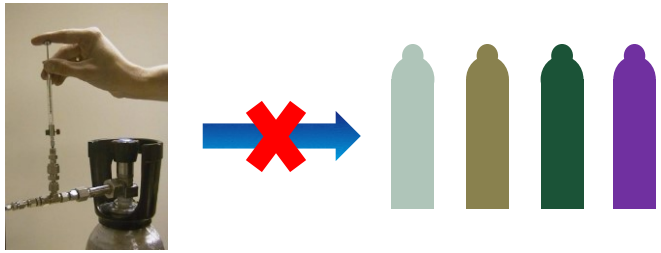
- Selected amine components and their physical properties

- Selected amine components
  - Methyldiethanolamine (MDEA)
  - Diethanolamine (DEA)
  - Monoethanolamine (MEA)
  - Piperazine (PZ)
  - Diglycolamine (DGA)
- Not feasible to prepare gas mixtures in high Pressure gas cylinders.



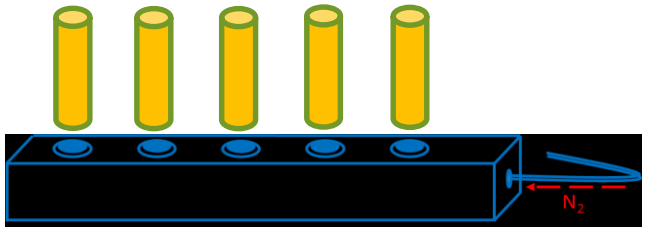
	MEA	Piperazine	DGA	DEA	MDEA
Molar mass (g/mol)	61.08	86.14	105.14	105.14	119.16
Density (g/mL)	1.01	1.1	1.048	1.1	1.04
Boiling point (°C)	171	145-148	218-224	271	247
Vapour pressure (kPa 20 °C)	0.064	0.021	< 0.01	< 0.001	0.001
CAS	141-43-5	110-85-0	929-06-6	111-42-2	105-59-9

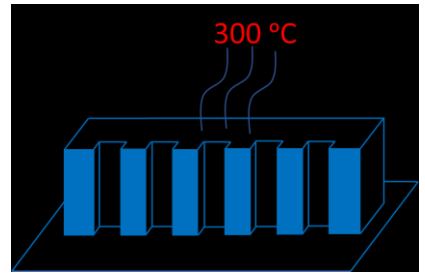
- Spike liquid amine mixtures on sorbent tubes (as transfer standard)



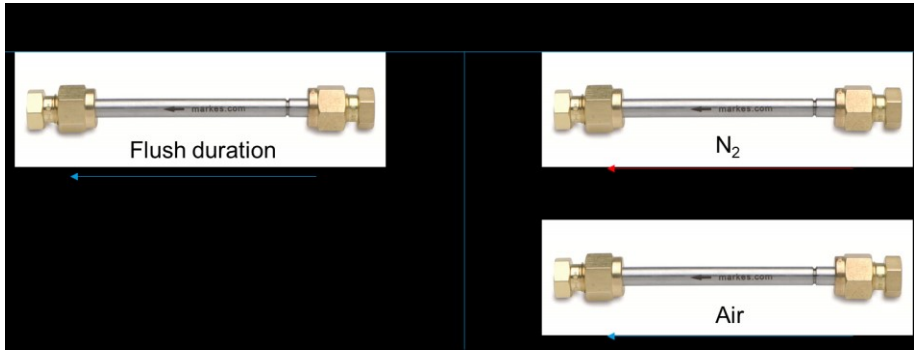
Development of measurement standards
- Procedure and Tested parameters

- Procedure
  - ✓Purity analysis of amine chemicals
  - ✓Preparation of liquid amine mixtures
  - ✓Cleaning of syringe prior usage
  - ✓Selection of sorbent tubes
  - ✓Cleaning and conditioning of the tubes prior usage
  - ✓Spike proper amount of liquid amine mixture on sorbent tubes





- Tested parameters
  - ✓Tube flushing duration (with fixed flow rate)
  - ✓Flushing gas media

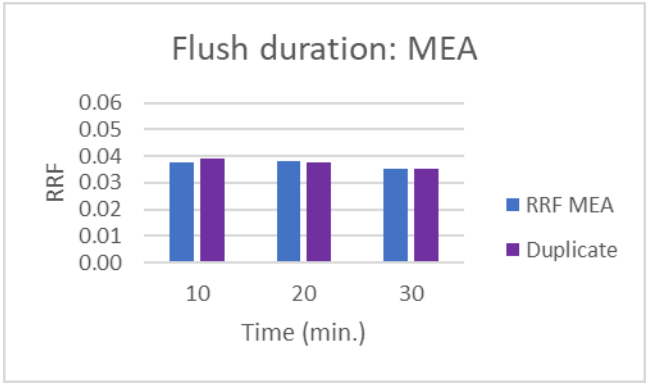


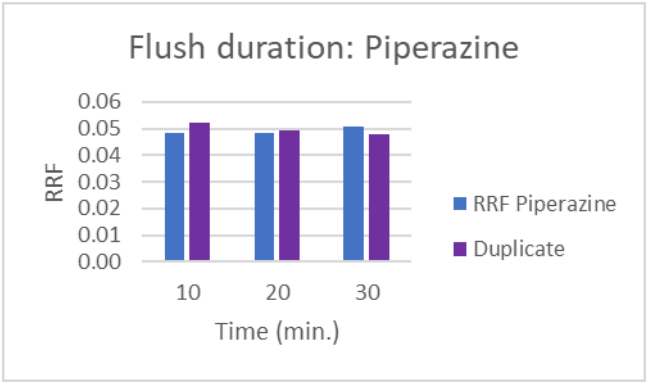
Development of measurement standards
- Effect of flushing duration

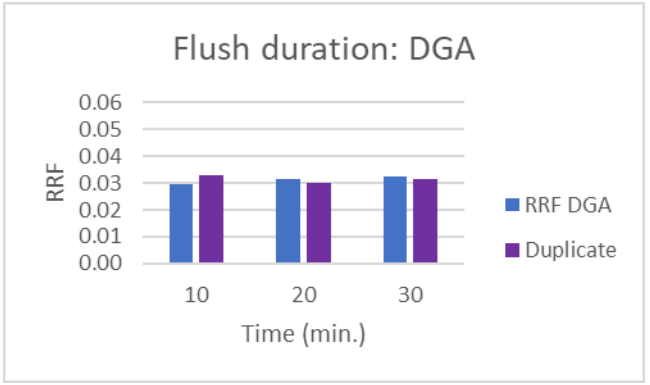
- Tested flush duration
  - 10min
  - 20min
  - 30min

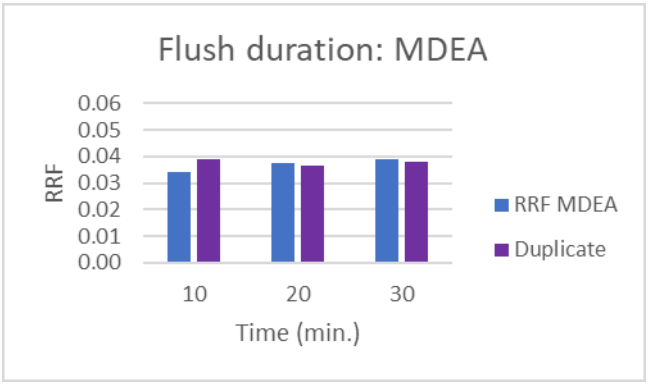
- *RRF* against internal standard is used

- Further experiments used 20min flush duration



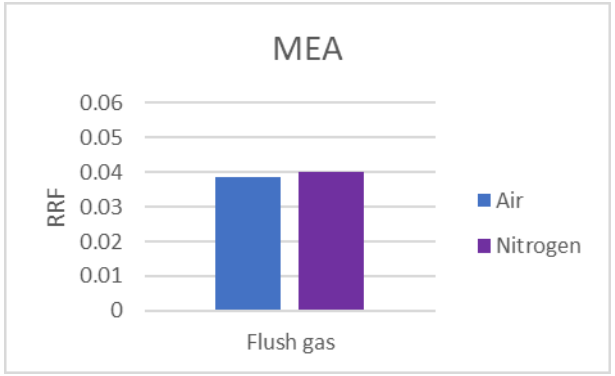


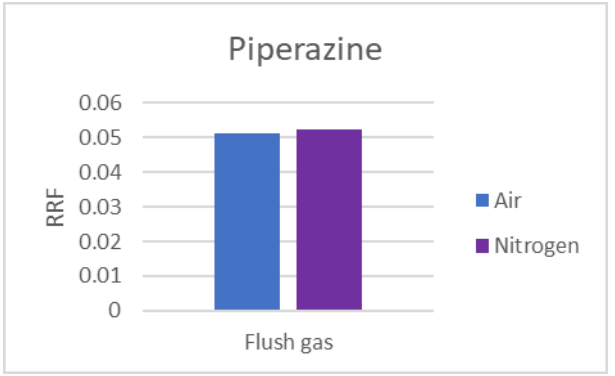


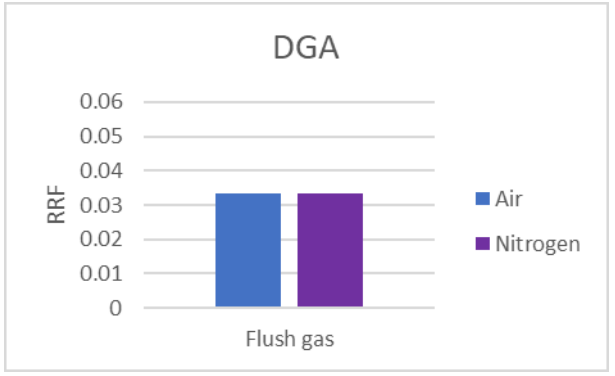


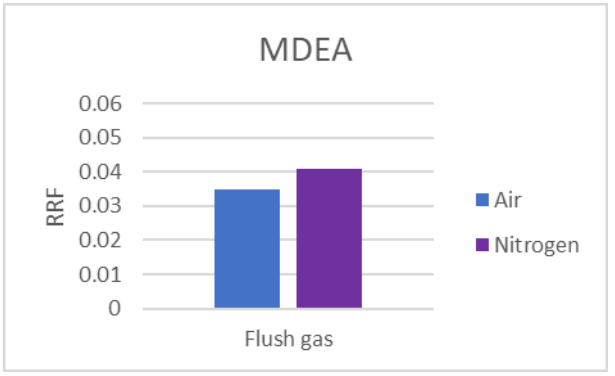
Development of measurement standards
- Effect of flushing gas media

- Tested flush gas media
  - Air (oxidation of amines)
  - Nitrogen
- *RRF* against internal standard is used
- Further experiments used nitrogen



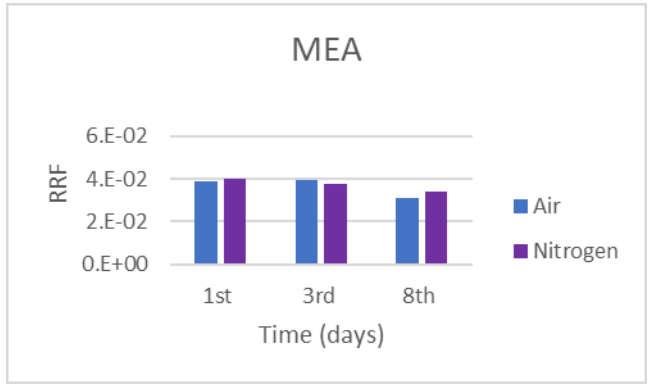


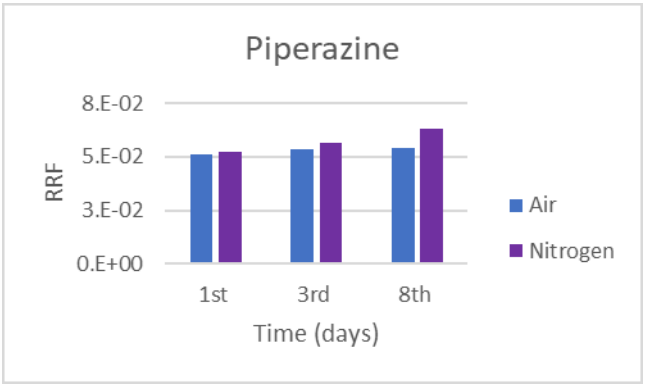


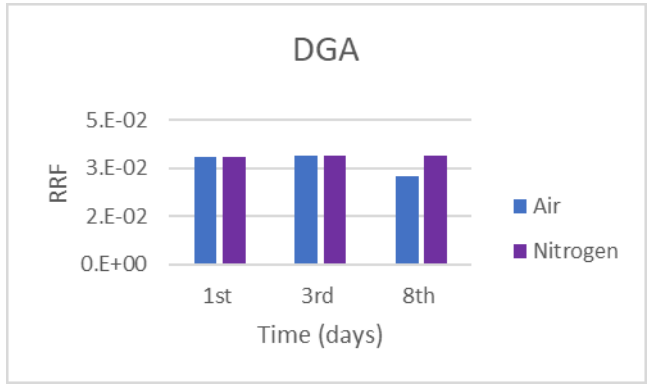


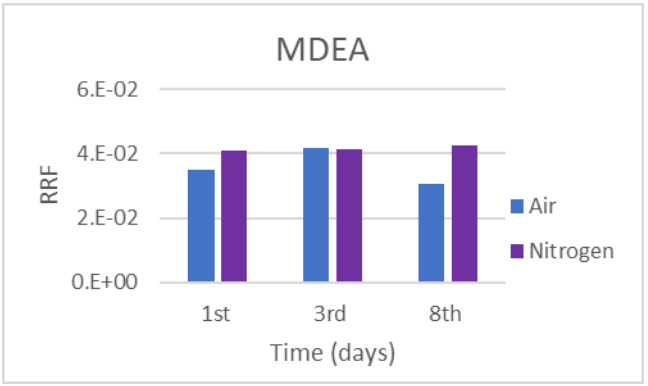
Development of measurement standards
- Stability test

- Short-term stability (1, 3, 8 days)
- Long-term stability up to 7 months
- Due to the poor reproducibility of the method and the large combined uncertainties, the long-term stability data do not show obvious trend.
- The combined uncertainty shall take into account:
  - the purity of the amine chemicals
  - the uncertainty on the weighing data
  - the miscibility of the solution
  - the uncertainty of the analysis including the tube spiking method



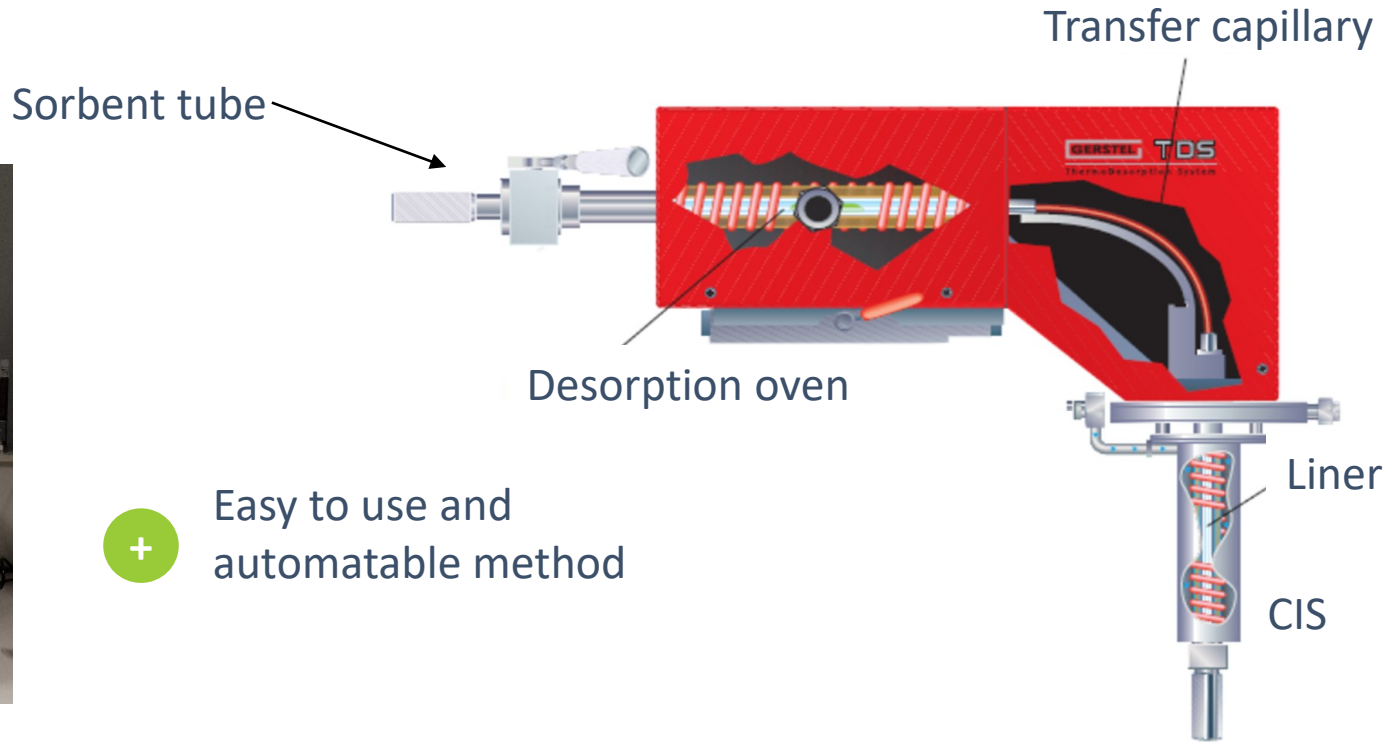






Development of analytical method
- TD-GC-MS

Selected method: Thermal Desorption (TD) - Gas Chromatography (GC) - Mass Spectrometry (MS)



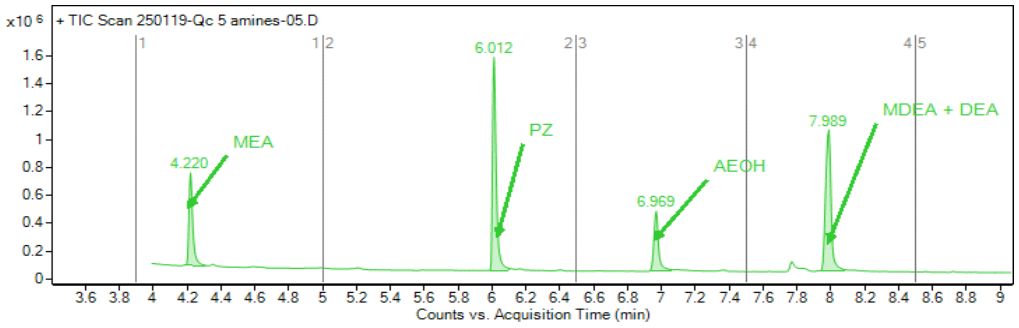
\+ Easy to use and automatable method

Development of analytical method
- Selection of the column

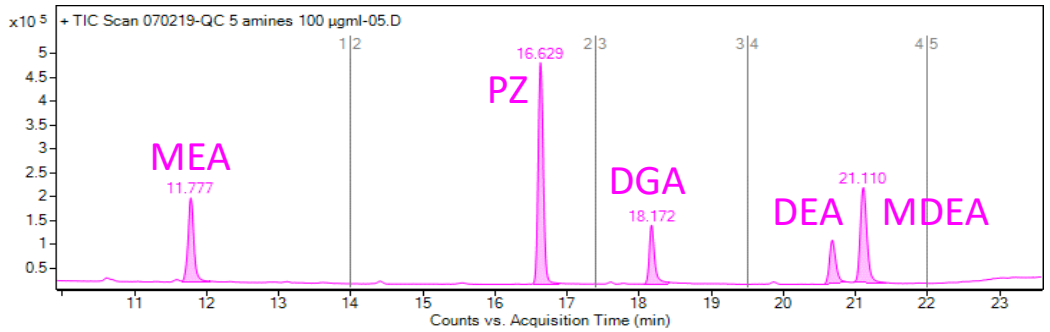
Three columns were tested and compared for their ability to separate the 5 amines:

- Rtx-Volatile Amine (30m x 0.32mm x 5µm)
- HP-5MS Ultra Inert (30m x 0.25mm x 0.25µm)
- DBWax (30m x 0.25mm x 0.5µm)

HP-5MS Ultra Inert column

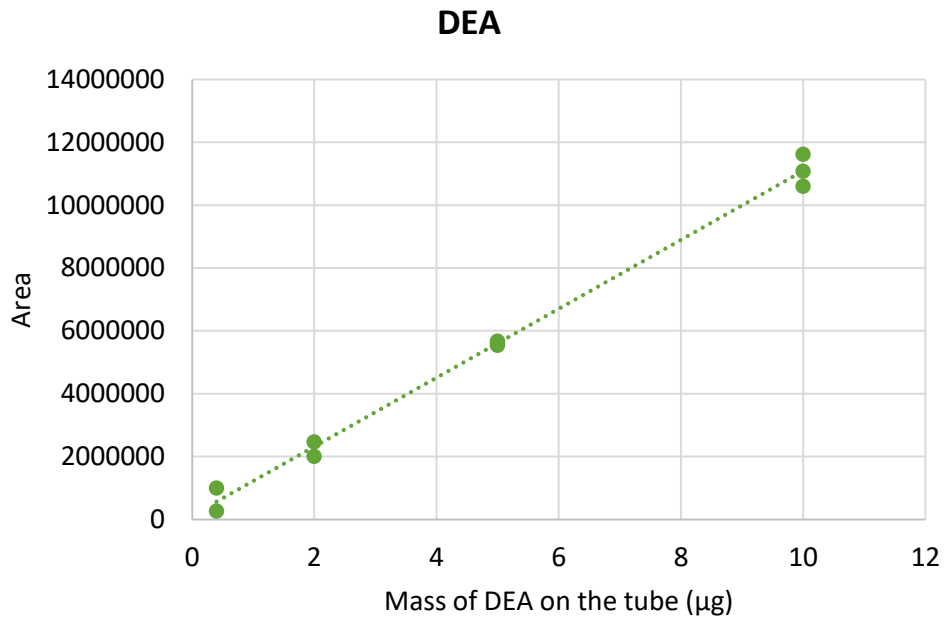


Rtx-Volatile Amine column



Rtx-Volatile Amine column was the most promising as it permitted a separation of the five amines in less than 25 minutes

Development of analytical method
- Characterization



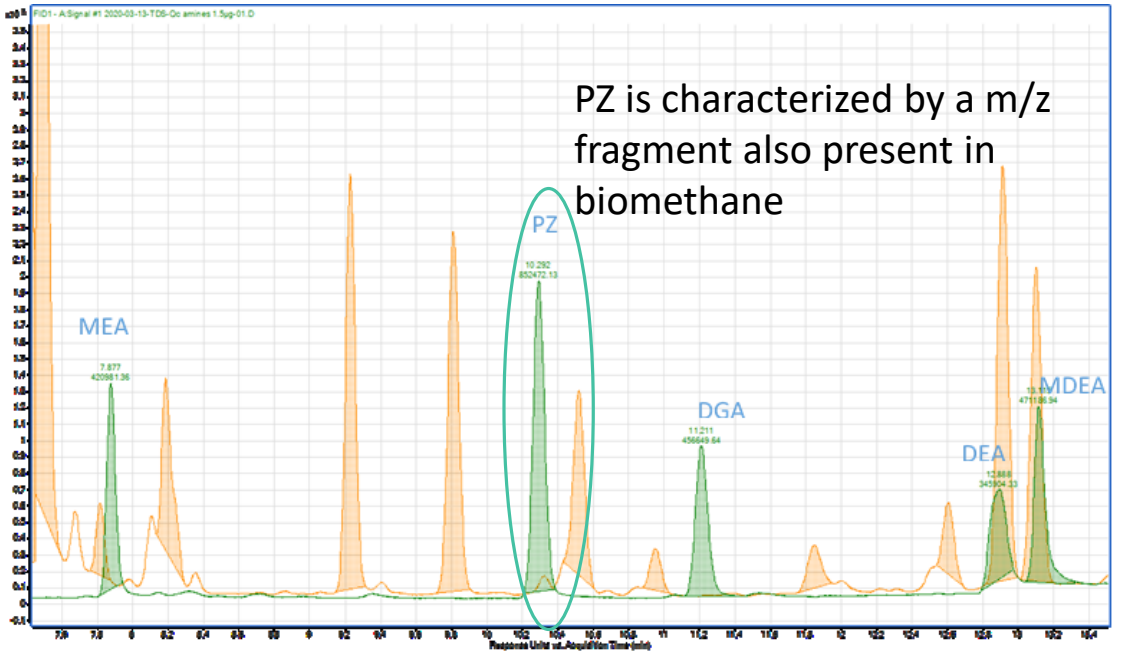
Linearity	Range of 0.4-10 µg on the sorbent tube
Repeatability	From 1.5 to 10 µg: RSD from 7 to 19% At 0.4 µg: RSD from 10 to 75%
LOQ	PZ & MDEA: 0.03 µg MEA, DGA & DEA: 0.1 µg
Accuracy	From 11% (PZ at 6 µg) to 42% (MDEA at 1.5 µg)
Uncertainties estimations	From 29% to 90%
Method specificity	FID: interferences with other components of biomethane MS SIM: not adapted for PZ monitoring

Further development is needed in order to improve the uncertainties of the analytical method.

Development of analytical method
- Real biomethane analysis

- RICE investigated for biomethane coming from amine based biogas purification, without success.
- A real biomethane was analyzed, but it did not came from an amine purification process.
- Two chromatograms were overlaid: real biomethane and amines.

The use of MS detection is necessary to avoid interferences with other components of biomethane (except for PZ for which further development is needed).



Conclusions

- Measurement standards containing five amines were prepared on Tenax TA sorbent tubes.
- The short-term (up to 8 days) and long-term stability (up to 7 months) tests were performed.
- Two TD-GC-MS methods were developed and characterized by GRTgaz RICE and VSL.
- Further research is needed in order to reduce the uncertainties of the methods.
- However, there is no pressing need expressed yet from the stakeholders committee to monitor these amine components accurately.

Acknowledgement

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