

**Analytical methods for
measuring amines**

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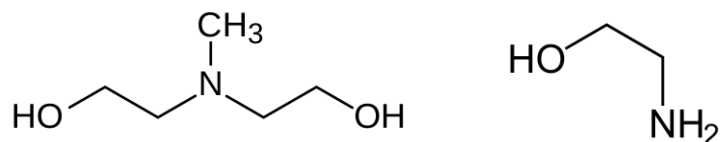
+ Amines and biomethane: context

Biogas from anaerobic digestion is mainly composed of methane, CO₂, and trace components (i.e. hydrogen sulfide, siloxanes, ammonia, ...).

Biogas upgrading into biomethane is performed by:

- + Cleaning process to remove CO₂ and trace components:

↳ Chemical absorption using **amines solvents**



Need to monitor their presence in biomethane

- + Upgrading process to adjust the calorific value





Amines and biomethane: context

EN 16723-1 norm specifies a limit of 10 mg/m³ for amines

Parameter	Unit	Limit values ^a		Test method (Informative)
		Min	Max	
Total volatile silicon (as Si)	mgSi/m ³		0,3 to 1 ^b	EN ISO 16017-1:2000 TDS-GC-MS
Compressor oil		c		ISO 8573-2:2007
Dust impurities		c		ISO 8573-4:2001
Chlorinated compounds		-	d, e	EN 1911:2010
Fluorinated compounds			d	NF X43-304:2007 ISO 15713:2006
CO	% mol	-	0,1 ^f	EN ISO 6974- series
NH ₃	mg/m ³		10	NEN 2826:1999 or VDI 3496 Blatt 1:1982-04 NF X43-303:2011
Amine	mg/m³		10	VDI 2467 Blatt 2:1991-08

+ Amines and biomethane: context

Metrology for Biomethane project : 2 tasks dedicated to amines

WP1, Task 1.4: Measurement standards for amines

- + Development of stable amines measurement standards + accurate analytical method to monitor their stability



WP3, Task 3.6: Test method for amines in biomethane

- + Development and validation of standardized methods for the monitoring of amines in biomethane.



+ Task 1.4: Measurement standards for amines





The aim of this task is to develop measurement standards for the amine content in biomethane.

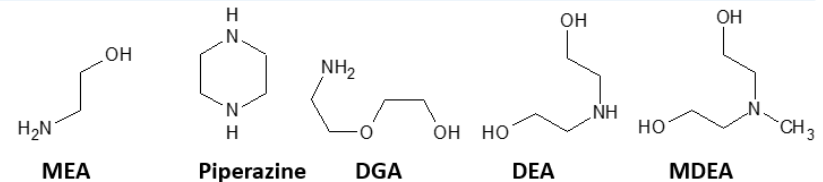
Activity number	Activity description	Partners (Lead in bold)
A1.4.1	<ul style="list-style-type: none">- Selection of at least 2-3 amines using information from the literature and from current European practices (i.e. gas treatment using amines).- Specification of the ranges of the components that will be studied	VSL , RICE GRTgaz
A1.4.2	<ul style="list-style-type: none">- VSL will prepare a suite of 5 multicomponent gravimetric biomethane gas mixtures with varying amines content.	VSL
A1.4.3	<ul style="list-style-type: none">- RICE GRTgaz will develop, with the help of VSL, a reference analytical method for the verification of the composition of the amine standards prepared in A1.4.2 using GC/MS and GC/FID.	RICE GRTgaz , VSL
A1.4.4	<ul style="list-style-type: none">- VSL, with support from RICE GRTgaz, will implement the method developed by RICE GRTgaz in A1.4.3 and will assess the stability of the amines in biomethane measurement standards prepared in A1.4.2.	VSL , RICE GRTgaz
A1.4.5	<ul style="list-style-type: none">- VSL with support from RICE GRTgaz will provide a full uncertainty budget for the at least 4-5 amines in biométhane.	VSL , RICE GRTgaz
A1.4.6	<ul style="list-style-type: none">- Writing of the report.	VSL , RICE GRTgaz

+ Task 1.4: Amines selection

Activity 1.4.1 VSL and RICE GRTgaz will select at least 2-3 amines using information from the literature and from current European practices (i.e. gas treatment using amines). They will then obtain the selected amines and specify the ranges of the components that will be used in the measurement standards in A1.4.2. The starting point will be the target range of 5 ppm to 100 ppb. (VSL, RICE GRTgaz, June 2017 – July 2017)

- Literature study
- Select of components (**4-5 amines** based on request in A1.4.5)
 - ✓ methyldiethanolamine (MDEA)
 - ✓ diethanolamine (DEA)
 - ✓ monoethanolamine (MEA)
 - ✓ piperazine (PZ)
 - ✓ diglycolamine (DGA)
- Confirm concentration range

AMMONIA	PRIMARY AMINE	SECONDARY AMINE	TERTIARY AMINE
$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{N}}}-\text{H}$	$\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{N}}}-\text{H}$	$\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{N}}}-\text{R}'$	$\text{R}-\overset{\text{R}'}{\underset{\text{R}'}{\text{N}}}-\text{R}'$
			
NH_3	CH_3-NH_2	$\text{CH}_3-\text{NH}-\text{CH}_3$	$\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}}}-\text{CH}_3$

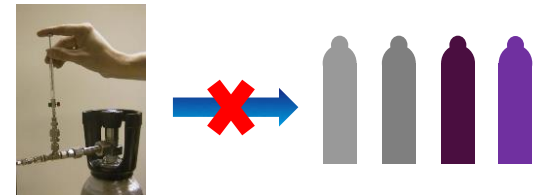


Molar mass (g/mol)	61.08	86.14	105.14	105.14	119.16
Density (g/mL)	1.01	1.1	1.048	1.1	1.04
Boiling point (°C)	171	145-148	218-224	271	247
Vapour pressure (kPa 20 °C)	0.064	0.021	< 0.01	< 0.001	0.001
CAS	141-43-5	110-85-0	929-06-6	111-42-2	105-59-9

+ Task 1.4: Measurement standards preparation

Activity 1.4.2 Using input from A1.4.1, VSL will prepare a suite of 5 multicomponent gravimetric biomethane gas mixtures with varying amines content (as specified in A1.4.1) using its facilities for gravimetric liquid and gas mixture preparation. This will demonstrate if the range proposed in A1.4.1 is feasible. (VSL, Aug 2017 – Nov 2017)

- Physical property checking
- Feasibility of liquid and gas mixture preparation
 - Not feasible for gas mixture preparation in cylinders
 - Will spike liquid amine mixtures on sorbent tubes
 - Sorbent tubes as transfer standard
- Purity analysis of amine chemicals
- Select candidate sorbent tube type (coated Tenax TA)
- Select component to be used as internal standard (n-octane)



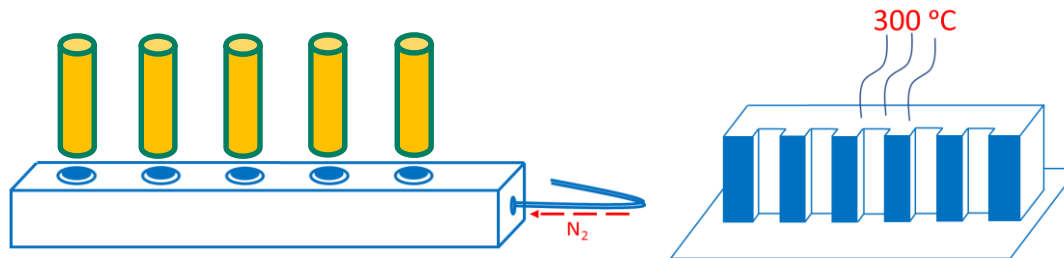
Parameter TD tubes



+ Task 1.4: Analytical method development

Activity 1.4.3 RICE GRTgaz will develop, with the help of VSL, a reference analytical method for the verification of the composition of the amine standards prepared in A1.4.2 using GC/MS and GC/FID. At 5 ppm, the target expanded uncertainty will be approximately 3 % - 4 % and at 100 ppb, the target expanded uncertainty will be approximately 5 %. (RICE GRTgaz, VSL, Dec 2017 – May 2018)

➤ Develop analytical method using (TD)-GC-MS/FID



+ Task 1.4: Analytical method development

1 Sampling on solid sorbent

Aim: Preconcentrate potential amines at trace level in biomethane (WP3)



Adapted for on-site use



Easy to use method

Preconcentration method

Amines in biomethane would potentially come from the purification step of biogas with Amine scrubbing.



In the field of CO₂ capture process with amine absorption, **Tenax® TA** sorbents have shown promising results in terms of amines characterization of the treated flue gas.

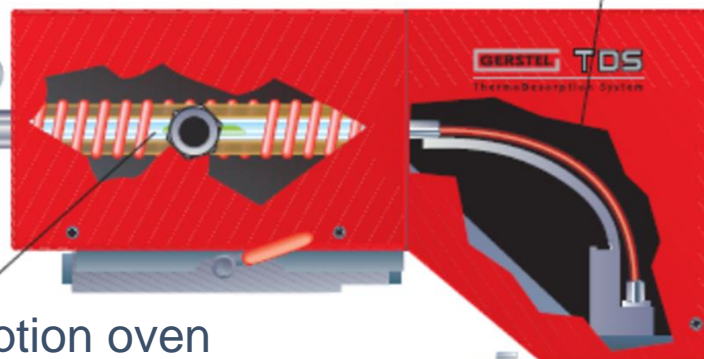
+ Task 1.4: Analytical method development

2 Desorption & Analysis by Thermal Desorption (TDS) - Gas Chromatography (GC) - Mass Spectrometry (MS)

Sorbent tube



Desorption oven



Transfer capillary



Liner

CIS

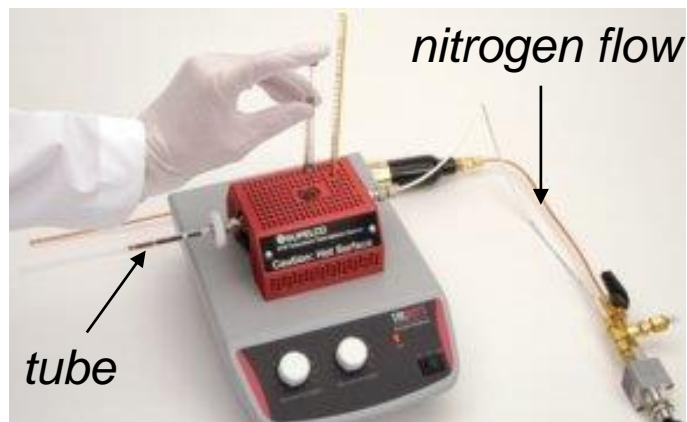


Easy to use and automatable method

+ Task 1.4: Analytical method development

Calibration by spiking tubes with known amounts of amines:

ATIS™: Adsorbent Tube Injector System



- Injection of a small volume of solution (μL) in a heated chamber
- Trapping of the compounds on the solid sorbent of the tube

Direct liquid injection:

Injection of a small volume of solution on the sorbent itself

EN 16723-1 norm specifies a limit of 10 mg/m^3 for amines
Target range : $5 - 12 \text{ mg/m}^3$



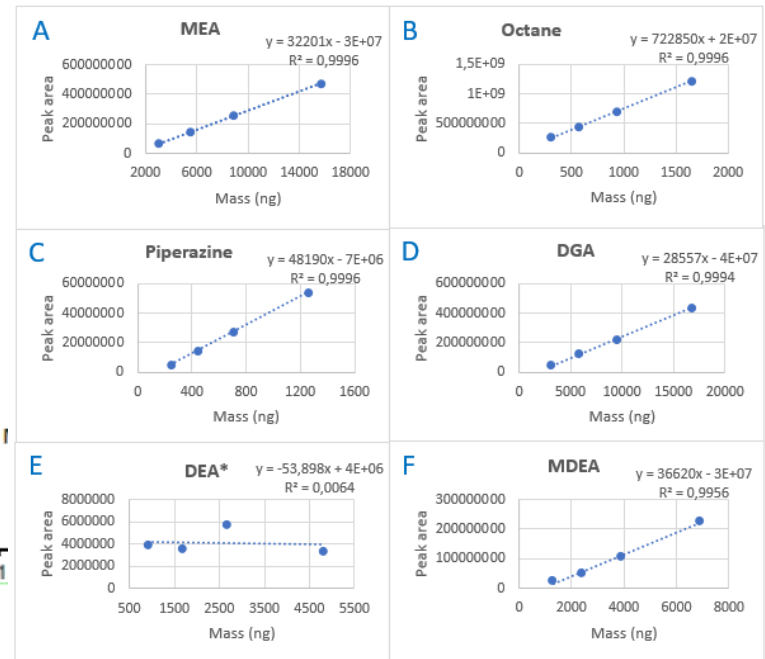
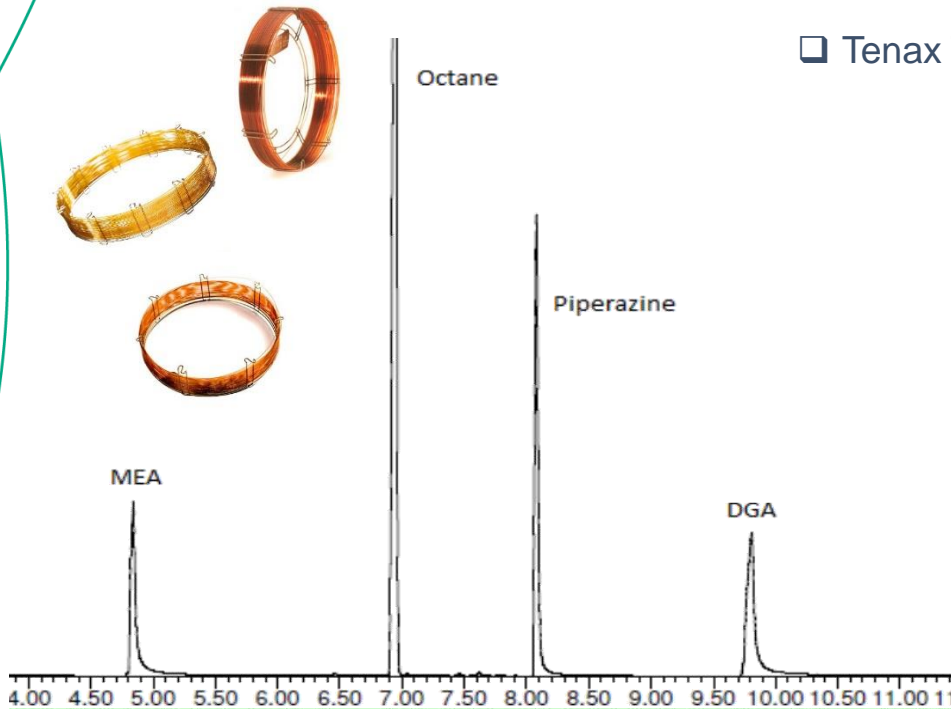
Monoethanolamine's (MEA) and Piperazine's (PZ) spiking might be challenging because of their volatility.

+ Task 1.4: Analytical method development

VSL has tested 3 different GC columns. Tests with another column is planned. Method improvement is on-going.

Tools:

- TD-GC-MS/FID
- Tenax TA sorbent tubes



+ Task 1.4: Uncertainty budget and report

Activity 1.4.5 VSL with support from RICE GRTgaz will provide a full uncertainty budget for the at least 4-5 amines in biomethane, based on the experience gained from EMRP JRP ENG01 and ENV56 and supplemented by the stability data obtained in A1.4.4. (**VSL**, RICE GRTgaz, Nov 2019 – Jan 2020)

- Stability data report
- Full uncertainty budget

Activity 1.4.6 VSL with support from RICE GRTgaz will use the results from Task 1.4 to prepare D4, and the coordinator will then submit the report to EURAMET as D4: 'Report on the development of the measurement standards, a validated calibration method for the measurement of amines content in biomethane and a relative expanded uncertainty of 5 %'. (**VSL**, RICE GRTgaz, Dec 2019 – Mar 2020)

- Report of D4

+ Conclusions: VSL activities

- ❑ **Development of measurement standard for amine components**
 - Gravimetric gas standard in cylinders is not feasible due to physical properties of selected amines
 - Development of standard by spiking amines on Tenax TA TD tubes, various parameters have been tested
 - TD tube flushing duration (10, **20**, 30min)
 - TU tube flushing gas (**nitrogen** and air)
 - Amines spiking amounts on the tubes (range needs to be optimised)
- ❑ **Development of analytical method for measuring amine components**
 - Purity analysis
 - Selection of GC columns
 - Current method repeatability ($\approx 5\%$ except for DEA)
 - Current method reproducibility (not good enough, $\approx 20\%$)
 - Current method linearity (good, except for DEA)
- ❑ **Stability tests**
 - Short-term stability study is performed (1, 3, 8 days)
 - Long-term stability study is to be carried out (up to 12 months)

+ Conclusions: RICE activities

WP1: In association with VSL, RICE will develop and validate an accurate method for the monitoring of the stability of 5 amines measurement standards.

WP3: RICE will need to perform analysis on a biomethane from an amine process purification



Any contact to provide samples?

The development of the amines method by RICE will be performed in 2019, taking advantage of its knowledge in the field of biomethane analysis.





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Any Questions?

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