Measurement techniques and test methods for measuring ammonia content

Workshop on conformity assessment of biomethane

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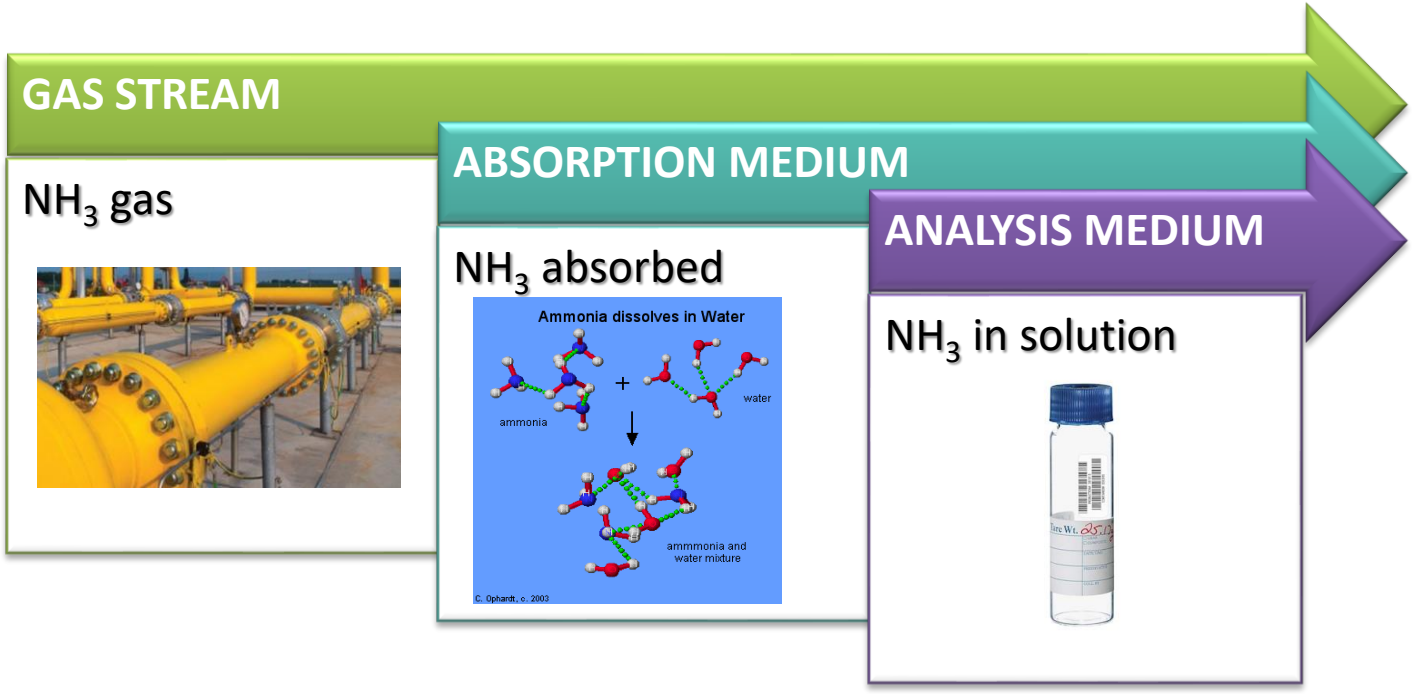
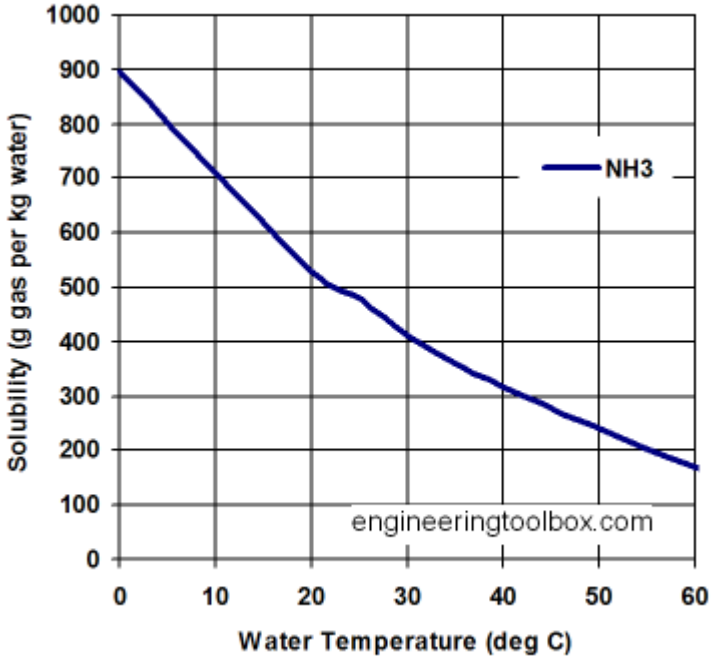
Ammonia sampling by absorption

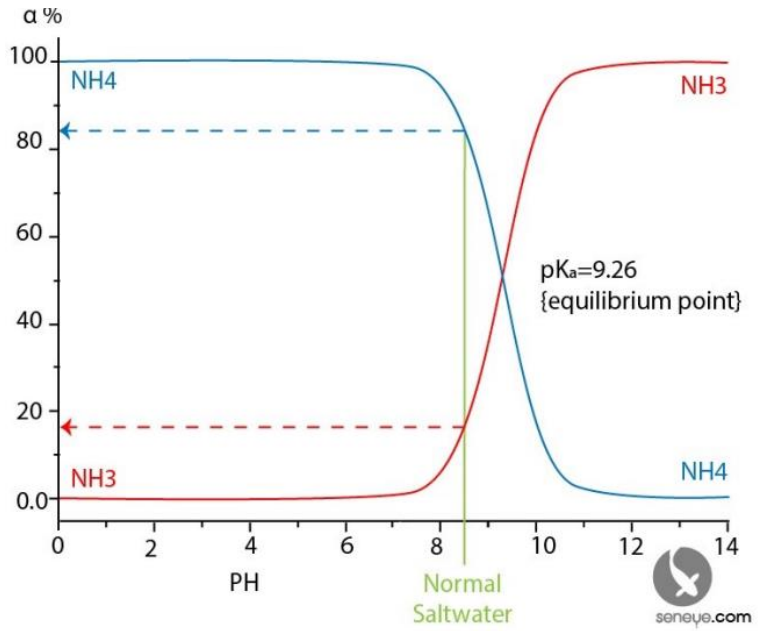


- ✓ **Absorption methods, in solution or on cartridge, are widely used in air quality and in-stack measurements**
- ✓ **EPA CTM 027, NIOSH 6015 , NIOSH 6016 and OSHA ID188 methods can be used as starting points for developing a suitable method for the sampling and analysis of ammonia in bio-methane**

Ammonia solubility in water

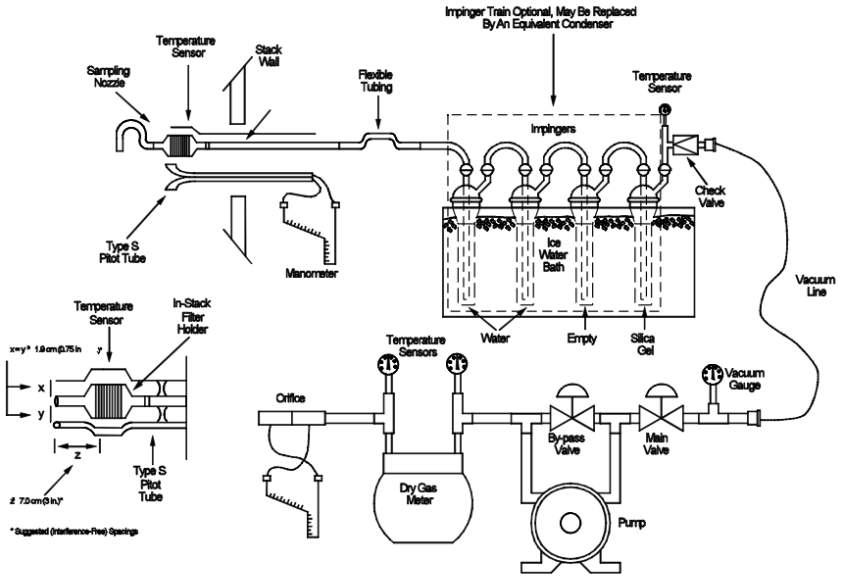


$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_{4(aq)}^{+} + OH^{-}_{(aq)}$$



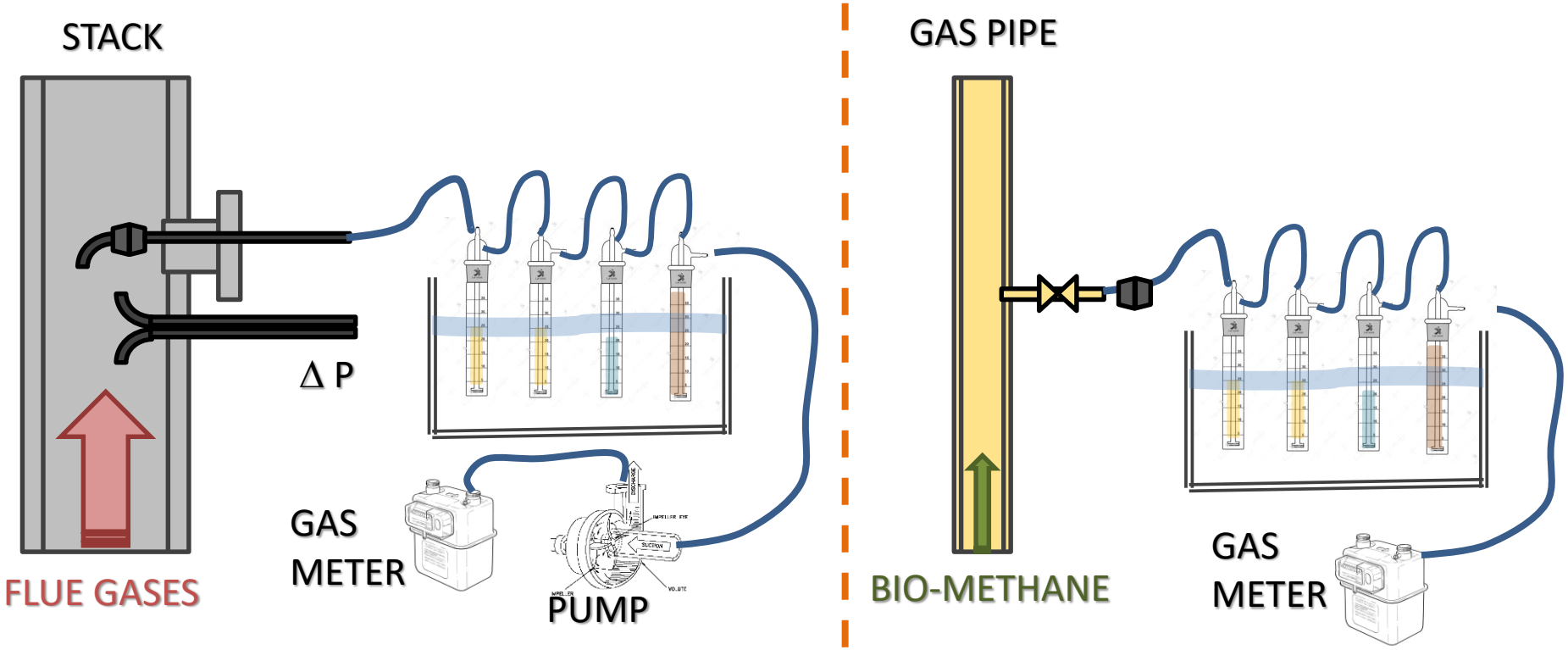
- ✓ **Ammonia has a very high solublity in water, mainly at low temperatures**
- ✓ **In acidic conditions mainly ammonium ions are present and a higher solubilisation of ammonia gas can be achieved**
- ✓ **A complete absorption of ammonia in water can be easily attained by bubbling the gas : this is the starting point of EPA CTM 027 method**

EPA CTM 027



- ✓ **The sampling train is the typical setup used for in-stack sampling using impingers**
- ✓ **It consists of a nozzle and a filter holder to collect particulate matter, placed in the stack, a set of four impingers in an ice-water bath and then a pump and a gas meters to quantify the amount of gas sampled. A pitot tube is used to maintain isokinetic conditions**

EPA CTM 027 vs Bio-methane Sampling Train



- ✓ **Isokinetic conditions for sampling can be neglected for bio-methane, as well as the filter**
- ✓ **A suction pump can be unnecessary, if the gas pressure is enough to maintain a stable bubbling flow in the impingers and to overcome the resistance of the gas meter**

Sample Preparation and Storage

1ST IMPINGER

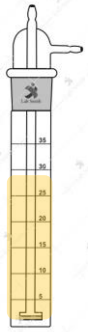
100 ml H_2SO_4 0,1N

RINSES

1ST SAMPLE BOTTLE

≈90% NH_3

2ND IMPINGER



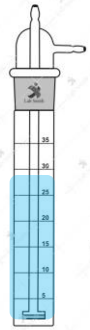
100 ml H_2SO_4 0,1N

RINSES

2ND SAMPLE BOTTLE

<10% NH_3

3RD IMPINGER



Empty or 100 ml H_2SO_4 0,1N

RINSES

3RD SAMPLE BOTTLE

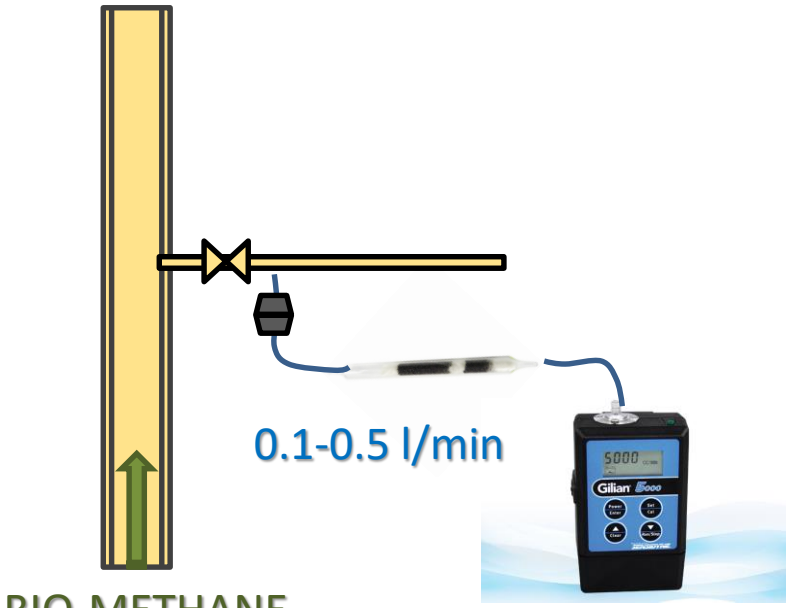
STORE AT 4 °C
2 weeks Max

- ✓ **Impingers solutions are transferred in HDPE bottles along with the rinses**
- ✓ **The first and second bottles have to be analysed, while the third only in the case ammonia breakthrough has occurred**

NIOSH 6015/6016 – OSHA D188 Sampling

TUBES WITH SILICA GEL or CARBON BEADS
Treated with H_2SO_4 can be used

GAS PIPE

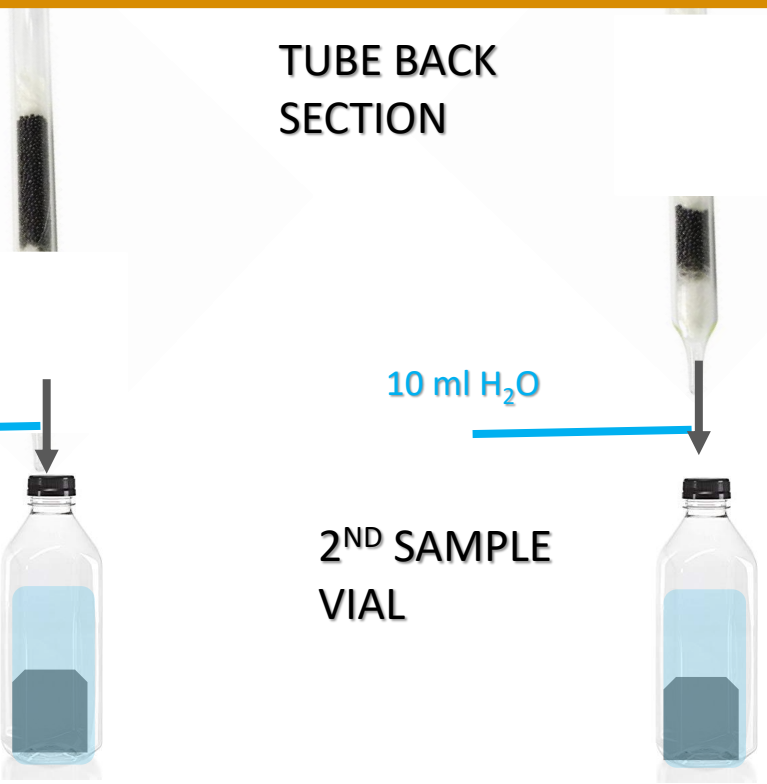


- ✓ **Ammonia can be collected with solid sorbent tubes**
- ✓ **Pre-filtering is optional, according to the expected particular matter content**
- ✓ **A personal sampling pump (available also in ATEX version) can be used**

Samples Preparation

TUBE FRONT SECTION

TUBE BACK SECTION



1ST SAMPLE VIAL

2ND SAMPLE VIAL

STORE TUBES
35 days at 5°C
1 day after desorption

- ✓ The two sections of the tubes are desorbed in water separately
- ✓ Analytical samples are analised along with field blanks

Concentration Range in Sampling Solutions

IMPINGERS METHOD

BIO-METHANE			SAMPLING		SOLUTION	
NH_3	10 *	mg/m3	rete	1 l/min	Volume	400 ml
			time	30 min	$C_{NH3\ sol\ max}$	1,36 mg/l
			Volume	30 l	$C_{NH3\ sol\ min}$	0,14 mg/l
			NH_3 tot.	0,3 mg		

SOLID SORBENT METHOD

BIO-METHANE			SAMPLING		SOLUTION	
NH_3	10 *	mg/m3	rete	0,2 l/min	Volume	10 ml
			time	30 min	$C_{NH3\ sol\ max}$	6,00 mg/l
			Volume	6 l	$C_{NH3\ sol\ min}$	3,00 mg/l
			NH_3 tot.	0,06 mg		

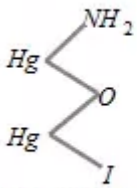
*** Limit value in EN 16723-1**

- ✓ **The range depends on many factors: the concentration of ammonia in bio-methane, the sampling rate, the sampling time and the amount of solvent used**
- ✓ **If higher concentrations are reached they can be easily reduced by dilution, while higher sampling times and rates can be set when lower values are expected**

Analytical Techniques

NESSLER'S REAGENT TEST

$$2K_2HgI_4 + NH_4Cl + 4\,KOH \longrightarrow$$

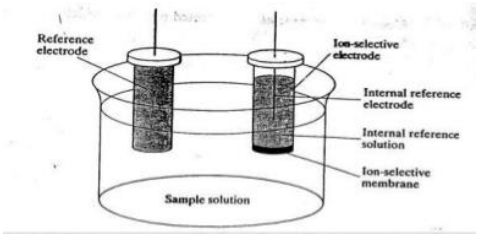


$$+ 7\,KI + KCl + 3H_2O$$

Iodideof Million'sbase (Brownppt.)

COLORIMETRIC QUANTIFICATION

AMMONIA ION SELECTIVE ELECTRODE



typical range: 0.02 to 17000ppm.

- ✓ **Ammonia can be analyzed by a colorimetric method using Nessler reagent. This method has significant interferences. A disadvantage is that only clear solutions can be processed**
- ✓ **Another method, having a good operative range, uses ammonia ion specific electrode, which does not discriminate between ammonia and amines**

IC Method

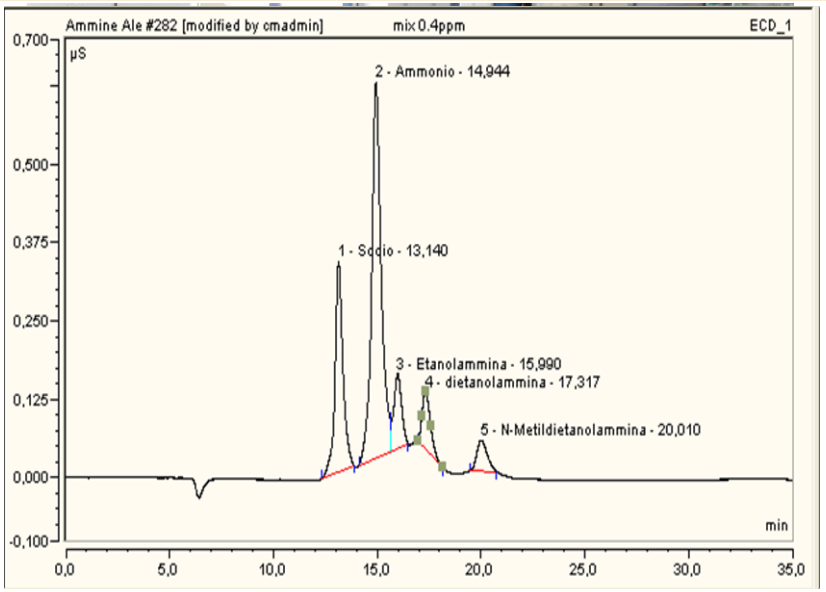
ION CHROMATOGRAPHY

Analysis performed by ICS 2500 ion chromatographic system (Dionex) consisting of:

- gradient pump (GS50),
- a chromatographic oven (LC 25),
- electrochemical detector (ED50),
- CSRS-4-mm Cation Suppressor
- Column CS20 4x250 mm

Analysis conditions:

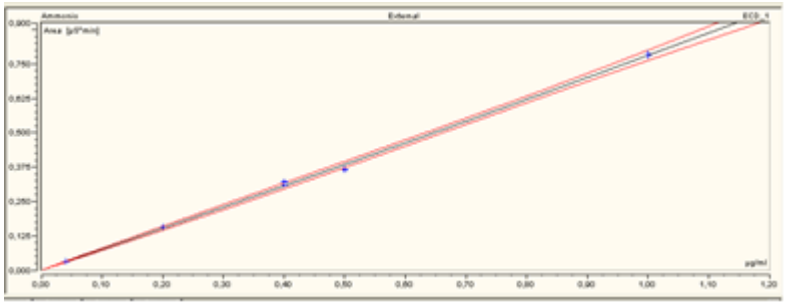
- oven temperature 30°C
- run time 35 min
- MSA 13 mM
- Flow 0.4 ml/min
- Suppressor Current 16 mA



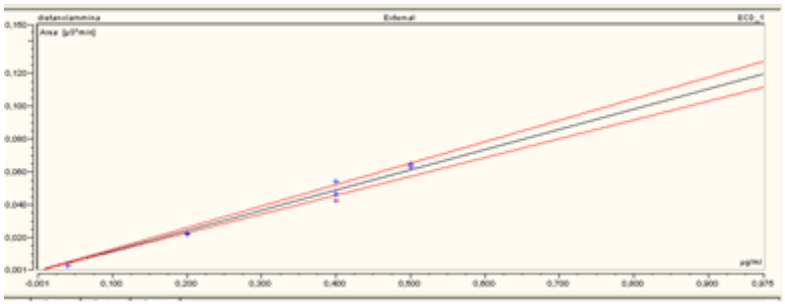
- ✓ **Ion Chromatography is a very common and straightforward method for quantifying ammonia in water solutions**
- ✓ **Possible interference is due to volatile amines peaks that can overlap the ammonia peak**
- ✓ **If amines peaks can be properly separated, IC may be a useful tool for quantifying ammonia and low MW amines in the same analysis**

IC Calibrations

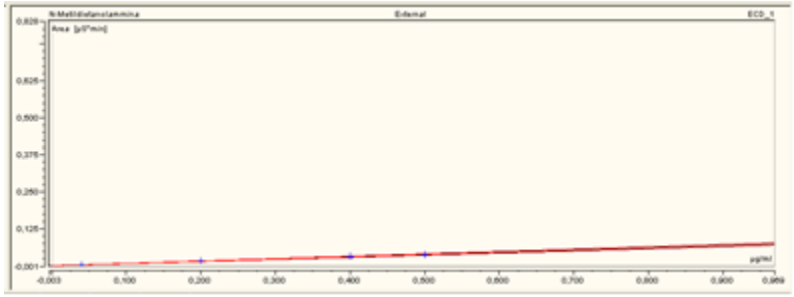
AMMONIA



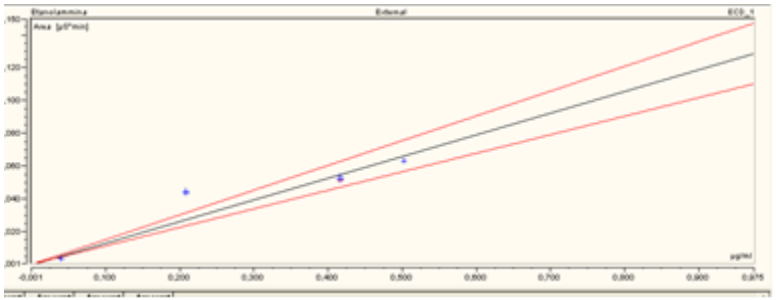
DIETHANOLAMINE



N-METHYLETHANOLAMINE



ETHANOLAMINE



No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev.	Coeff.Det.	Offset	Slope	H-V LOD	Curve
				%	%			µg/ml	
1	Ammonium	Quad	11	3.5757	99.8	0	0.7541	n.a.	0.0267
2	Ethanolamine	Lin	9	20.7011	85.5856	0	0.1319	n.a.	0
3	Dietahnolamine	Lin	9	10.0566	97.7338	0	0.1225	n.a.	0
4	N-Methildiethanolamine	ALin	8	4.234	99.6356	0	0.076	n.a.	0

IC Repeatability

	Amount µg/ml Ammonio	Amount µg/ml Etanolammina	Amount µg/ml dietanolammina	Amount µg/ml N-Metildietanolammina
test 1	0.23	0.28	0.09	0.15
test 2	0.23	0.31	0.09	0.11
test 3	0.22	0.27	0.08	0.15
test 4	0.22	0.26	0.09	0.11
test 5	0.22	0.25	0.07	0.15
test 6	0.22	0.26	0.08	0.10
test 7	0.22	0.26	0.08	0.14
test 8	0.22	0.27	0.07	0.12
test 9	0.22	0.27	0.09	0.15
test 10	0.24	0.32	0.07	0.18

average	0.23	0.27	0.08	0.13
std dev	0.007	0.024	0.008	0.026

- ✓ **Good repeatability, at the lower concentration range, is achieved for ammonia**
- ✓ **An acceptable repeatability is observed also for other amines present in bio-methane**
- ✓ **Higher MW amines are not detectable in IC under the operating conditions used in these tests**

CONCLUSIONS

- Absorption techniques are an easy and low cost way to sample ammonia in bio-methane streams
- Several analytical techniques are available and well consolidated for the quantification of ammonia in solution
- Potentially any laboratory has the possibility to perform the analysis of ammonia in bio-methane adopting these techniques
- They represent a good solution for the characterization of bio-methane in the field on a routine base
- IC is the more suited analytical technique to prevent interferences from other amines, if a good separation can be achieved
- IC is potentially useful for the simultaneous quantification of ammonia and low MW amines in bio-methane
- Further validation with standard cylinders have to be carried out before the end of the Project

For Further Information

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