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ANALYSIS AND SAMPLING METHODS -POST-COMBUSTION CO2 CAPTURE PROCESS

RAMBOLL

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1. INTRODUCTION

This report presents the current sampling and analysis methods developed by Ramboll Analytics for the volatile and non-volatile nitrosoamines, alkylamines, solvent amines, ammonia, formaldehyde and acetaldehyde emitting from the ducts and stacks. Methods may also be applied for the analysis of wash water and solvent in amine based post combustion capture processes (PCC). All methods are presented at the appendixes and can be used independently.

2. SCOPE

Methods described in this report and supplements determine the concentrations of nitrosoamine, alkylamine, solvent amine, ammonia, formaldehyde and acetaldehyde compounds in a flue gas of PCC facility.

Sampling is performed using ambient temperature probe and isokinetic sampling. Sample gas is cooled in condensate vessel and further conducted through the absorbent section and dried by silica gel and gas flow is measured. Methods are tested at the field conditions on PCC-plant, but Round Robin test for the full procedure has not been performed.

The method is applicable to waste gases emitted from the MEA based post combustion capture process, wash water and solvents in process. The concentrations in flue gas may vary under normal pressure and temperature conditions as follows:

Compound	**CAS**	**Max. MEA concentration the liquid sample**	**Detection limit µg/m³n, sample volume 0,5 m³n**	**Detection limit µg/l**	**Analysis method**
1,4-Dinitrosopiperazine	140-79-4	10 %	0.005	0.05	LLE / GC-HRMS
N-nitrosodiethylamine (NDEA)	55-18-5	10 %	0.005	0.05	LLE / GC-HRMS
N-nitrosodimethyl-amine (NDMA)	62-75-9	10 %	0.005	0.05	LLE / GC-HRMS
N-nitrosomorpholine (NMOR)	59-89-2	10 %	0.005	0.05	LLE / GC-HRMS
N-nitrosopiperidine (NPIP)	100-75-4	10 %	0.005	0.05	LLE / GC-HRMS
N-Nitrosopiperazine	5632-47-3	0,2 %	1	10	LLE / GC-HRMS
N-nitrosodiethanol-amine (NDELA)	1116-54-7	0,2 %	1	10	DI/ UPLC-MSMS
Diethylamine (DEN)	109-89-7	0,2 %*	1	10	DI (cond. and evap.)/UPLC-MSMS
Dimethylamine (DMA)	124-40-3	0,2 %*	1	10	DI (cond. and evap.)/UPLC-MSMS
Ethylamine (EA)	75-04-7	0,2 %*	1	10	DI (cond. and evap.)/UPLC-MSMS
Methylamine (MMA)	74-89-5	0,2 %*	1	10	DI (cond. and evap.)/UPLC-MSMS
Triethylamine (TEA)	121-44-8	0,2 %*	1	10	DI (cond. and evap.)/UPLC-MSMS
Trimethylamine (TMA)	75-50-3	0,2 %*	1	10	DI (cond. and evap.)/UPLC-MSMS
2-amino-2-methyl-1-propanol (AMP)	124-68-5	0,2 %*	1	10	DI/ UPLC-MSMS
Diethanolamine (DEA)	111-42-2	0,2 %*	3	20	DI/ UPLC-MSMS
1,2-diaminoethane (EDA)	107-15-3	0,2 %*	50	400	DI/ UPLC-MSMS
N-methyldiethanol-amine (MDEA)	105-59-9	0,2 %*	10	400	DI/ UPLC-MSMS
Monoethanolamine (MEA)	141-43-5	100 %	1	10	DI/ UPLC-MSMS
Piperazine	110-85-0	not evaluated	not evaluated	-	DI/UPLC-MSMS
Acetaldehyde	75-07-0	10 %	0.050	0.5	LLE/UPLC-MSMS
Formaldehyde	50-00-0	10 %	0.050	0.5	LLE/UPLC-MSMS
Ammonia	7664-41-7	0,2 %*	5 000	5 000	DI/HPLC-CD

**max. concentration not evaluated*

3. NORMATIVE REFERENCE

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13284-1:2001, Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report

EN ISO 3696:1995, Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)

4. TERMS AND DEFINITIONS

4.1 Abbreviations

AMP	2-Amino-2-methyl-1-propanol
DCM	Dichloromethane
DEA	Diethanolamine
DEN	Diethylamine
DI	Direct injection
DL	Detection Limit
DMA	Dimethylamine
EA	Ethylamine
EDA	1,2-Diaminoethane
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
IDL	Instrument Detection Limit
LMW	Low Molecular Weight
MDEA	N-Methyldiethanolamine
MDL	Method Detection Limit
MEA	Monoethanolamine
MeOH	Methanol, methyl alcohol
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
PCC	Post combustion CO_2-capture
RI	Refractive Index
SIM	Single-ion monitoring
SPE	Solid-Phase Extraction
T_b	Boiling point
TMA	Trimethylamine
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
vis	Visible

4.2 Terms and definitions

4.2.1 Solvent amine(s)

Common name used in this study for alkanolamines.

4.2.2 Isokinetic sampling

Sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as the velocity and direction of the gas in the duct at the sampling point.

4.2.3 Analytical blank value

Value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all relevant reagents and materials.

4.2.4 Limit of detection (LOD)

Minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability.
The measurement value can be distinguished from the analytical blank value with a confidence of 99%, when the limit of detection is expressed as the mean analytical blank value plus three times the standard deviation of the analytical blank.
The limit of detection should preferably be calculated from the analytical blank. If this is not possible, the limit of detection can be calculated from the signal to noise ratio.

4.2.5 limit of quantification (LOQ)

Limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus five to ten times the standard deviation of the analytical blank. The limit of quantification should preferably be calculated from the analytical blank. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio.

5. DISCUSSION

This discussion part attempts to enlighten some main observations from the results gained from the pilot plant measurement campaign. Due to contractual reasons actual concentrations are not presented.

5.1 Sampling and storage

Tests with the isokinetic sampling gave relatively congruent results when analysing water concentration on flue gas using isokinetic and non-isokinetic sampling. However, a difference was observed on MEA concentration between the parallel samplings. About 50 % higher MEA concentration was measured on the sampling system with the lowest sampling rate and internal volume. One explanation is that absorption efficiency against MEA was higher on the smallest sampling train because of glass sinter tips on the bubblers end and slower velocity though the absorption solution. If this is the case, it means that a significant amount of MEA is not in the water droplets of the flue gas because measured water content equals between all three separate systems. Thus MEA behaves differently on the sampling compared to water and the solubility time shall be taken in account on sampling. On the high volume sampling trains bubble size in the absorber solution was significantly bigger than in the smallest under isokinetic sampling train. It is possible that MEA went partly through the system either gaseous form or as an aerosol. This is confirmed also in the other sampling tests where MEA amount in the absorber section was about the same as in the condenser.

Absorbent recoveries were tested on EPA 0011 based aldehyde sampling and measured acetaldehyde recoveries on three high volume absorbers in series were from first to third 91 %, 7 % and 2 % of overall amount in the absorbers.

Whatever the reason is, it has been observed e.g. during the validation of PCDD/F sampling that isokinetic sampling leads lower deviation between the samples and so the isokinetic sampling is recommended though it may not be significant factor on overall uncertainty.

During the field test it was observed that heating of the sampling system increased the concentration of degradation products such as nitrosoamines. This was observed on the temperature of 120 °C and formation was higher at temperature of 180 °C. When measuring humid flue gas, a filtering may be utilized only if filter is heated over dew point. In practise this means that filtering may not be recommended when measuring the PCC flue gas.

Effect of sulfamic acid in the condenser was tested in different ways e.g. by adding MEA into the condenser before the sampling. Solid sulfamic acid added into the condenser gave lowest result of nitrosamines after storage. On contrary condensate without sulfamic acid treated with NO_2^- yield formation of several nitrosamines on a significant level. Storage of these samples, even at temperature of –20°C, caused the formation of nitrosamines, up to 50 to 100 times higher, compared to the samples analysed immediately after the sampling. If sulfamic acid was added into the sample after the sampling there was no significant change on the nitrosoamine concentration during the storage although the samples were treated by NO_2^- before the storage.

On the samples with added sulfamic acid into the condenser before the sampling some nitrosoamines were detected level of detection limit. It is unsure if that is a result from background on relatively low level (~ng/m³n), existing result or formation of nitrosamines during the sampling. However, the pH value increased during the sampling up to 9. The effect of pH was not tested, but it is assumed that higher pH leads to higher formation rate of nitrosamines. It should be evaluated if the amount of sulfamic acid needs to be increased or alter the pH by some strong acid e.g. H_2SO_4.

Also other tests were performed. Alkalic sampling solution presented in the literature show poor absorption efficiency against the amines. Clean water was tested for absorption; it gave lower concentrations for MEA and alkylamines. Self-made absorbent tubes were tested by filling the cartridge normally used for the PCDD/F sampling with solid sulfamic acid and XAD-2 resin. On the analysis it was realized that background was poor and analysis were difficult to conduct without additional cleaning steps. Also XAD-2 resin coated with derivatisation agent 1-naphtyl isothiocyanate (or NIT) was tested similarly but the pre-treatment also proved to be a difficult task Theoretically this method could be used for additional detecting of ammonia and N-nitrosopiperazine but the pretreatment method would need additional development.

Thermosorb/N cartridges proved to be easy to analyse. Cartridges were mainly tested on heated filter tests because poor suitability on the emission measurements (expected low capacity against water and relatively low highest flow rate. Thermosorb/N looks good on non-humid atmosphere sampling such as work hygiene purposes. During the method development a detection limit of 0,2 ng/tube/single nitrosoamine compound was achieved.

Also Tenax TA and Carbopack B type thermal desorption tubes were tested; even those were known to be unsuitable for the emission measurements. On a typical thermal desorption temperatures standards gave more peaks than there was added compounds. On the real samples, several peaks were detected but the library search was unsuccessful and expected compounds were not detected on a reliable manner.

During the method development it was invented that 1.5 % formic acid/methanol solution would be an easy start for the further analysis. It has also good absorption for the alkyamines so it was selected for the absorbent testing. Also on real samples significant amount of tertiary trimethylamine was analysed from one sample. Tested absorbent is promising for the alkylamine sampling due to easy concentration step and retention also for tertiary amines unlike derivatization based methods. However, the absorption liquid above is flammable and so acidic water (0.1 M sulfamic acid) is presented as preferred method.

Ammonia was absorbed into boric acid solution and analysed ion chromatographically by an HPLC with conductivity detector.. Good correlation between FTIR and manual results were observed.

Results between DNPH cartridges and EPA 0011 method were comparable on aldehyde sampling. Small volume DNPH cartridges may suffer from high pressure drop on higher sampling rates or lack of capacity.

Eventually, recommended sampling system includes unheated SS316 steel nozzle and probe which are robust in field use. Unheated system includes continuous flushing during the sampling. Steel parts offer pre-cooling and non-absorptive circumstances during the sampling.

Chilled liquid absorption matrix has a good performance with some notices. Absorption efficiency should be determined for different type sampling construction; especially on solvent amine sampling. Condensation flask may need pre-cooler to avoid slip from the condensate flask to absorption vessels.

5.2 Nitrosoamines

Initially N-nitrosoamines were planned to be pre-treated with solid phase extraction (SPE) but the method was quite cumbersome and method did not work well when sample contained MEA. For volatile nitrosoamines the solution was to use liquid liquid extraction (LLE) with dichloromethane as the solvent. Dichloromethane is almost perfectly suitable for samples analysed with GC/HRMS and pretreated by LLE: It has relatively low boiling point and as it is heavier than water, it is easily separated and combined with earlier extractions. Also with LLE the matrix is not that problematic as ethanolamine is not substantially extracted with dichloromethane. Small amount of MEA which is extracted can easily be washed with water. Repeatable recoveries for LLE were tested to be between 30-100 %.

For the non-volatile nitrosoamines (in this case NDELA) the concentration step proved to be a difficult task as ideally most of MEA should be separated from NDELA to avoid problems in analysis phase. Initially SPE with Merck's LiChrolut EN seemed to be the method of choice for this compound, but it was found that the results were not repeatable. Recoveries varied significantly with sample volume, MEA concentration, pH-value and other reasons. Generally the recoveries were between 0-60 %. Other tested SPE phases were worse than LiChrolut EN. Also removal of MEA prior to concentration step was tested with cation exchange resin but the low capacity of the resin vs. the amount of MEA in the samples made this option unpractical. The use of silica was also mentioned in literature and several tests were conducted with commercial silica cartridges and also with self-made silica columns. Results were unsatisfactory and no substantial recovery was achieved.
Liquid liquid extraction was also tested with a selection of different solvents and combination of solvents in various pH values and sample/solvent volumes. From literature it was found that NDELA could be extracted with ethyl acetate in very acidic conditions, however this could not be verified. The use of acetonitrile/dichloromethane mixture was also promising at first as acetonitrile is almost completely extracted from water phase by dichloromethane but recovery of NDELA remained low. Finally and due to time limitations it was concluded that for now NDELA would be analysed with direct injection UPLC-MS/MS which worked well from typical flue gas sampling liquids.

5.3 Solvent amines

As a start point cation exchange SPE was tested for the solvent amines concentration step but it was concluded that the concentration in the samples is going to be high. Suitable dilution and direct injection to UPLC-MS/MS will be adequate for these compounds.

5.4 Alkylamines

The separation of alkylamines from MEA also proved to be a difficult task. Tests with cation exchange SPE showed that a concentration step for alkylamines (excluding trimethylamine) could be performed by this manner. However, this approach requires that MEA concentration is

relatively low i.e. in the same range as analytes. The problem with this SPE method is that the pKa values for MEA and alkylamines are too close to one another and they cannot be separated.

Also 1-naphtylisothiocyanate (NIT) derivatisation was tested but the basic problem was the same; only alkylamines cannot be derivatised excluding MEA. Additional problem with NIT derivatisation is that tertiary amines cannot be derivatized with NIT.

The most obvious difference between alkylamines and MEA is the boiling point: The separation of alkylamines from MEA with purge & trap methods were tested with very basic sample solutions acidic trapping solutions. This worked well with pure water but with MEA the recoveries decreased significantly (excluding trimethylamine).

Finally it was concluded that alkylamines may be analysed by direct injection to UPLC-MS/MS from all aqueous samples. Also acidic methanol solution can be concentrated by evaporation and can be used as an absorbent solution for alkylamines in flue gas sampling, but due to its flammability it is not preferred in field use.

5.5 Aldehydes

Aldehydes proved to be quite easily separated, concentrated and analysed. The reason for this is the selective derivatisation agent 2,4-dinitrophenylhydrazine (or DNPH) which does not react with MEA. For different sample matrices different approaches were selected. All aqueous samples are analysed with on-column derivatisation by Merck's LiChrolut EN cartridges. This method worked also with high MEA concentrations. For flue gas sampling there are two separate ways: Sampling into solid absorbent coated with DNPH or sampling with well-established EPA method. These both methods have pros and cons: Solid absorbent is less time consuming both before and after sampling but the capacity, pressure drop and dimensions of the cartridge makes it less suitable for flue gas sampling. EPA method is more time consuming in every step but the sampling can be easily applied for isokinetic sampling.

5.6 Ammonia

A Japanese industrial standard JIS K 0099:2004 was selected. It was tested at the pilot plant measurement campaign and proved to perform well.

5.7 Further steps

We propose the following steps for further studies:

- Round Robin sampling and analysis campaigns needs to be performed
- Methods to concentrate NDELA and alkylamines should be further developed
- Effect of other solvent matrix should be evaluated
- Labeled sampling standards should be tested and applied

APPENDIX 1
SAMPLING AND ANALYSIS OF NITROSOAMINES

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1. INTRODUCTION

This report presents the current sampling and analysis methods developed by Ramboll Analytics for nitrosoamines emitting from the ducts and stacks. Methods may also be applied for the analysis of wash water and solvent in amine based post combustion capture processes (PCC).

High concentration of solvent amine(s) in the sample may interfere on pretreatment and chromatographic separation of nitrosoamines. Performance of typical sample preparation processes may be seriously affected.

2. SCOPE

This method describes the sampling, extraction and analysis procedures of the studied nitrosoamines in monoethanol (MEA) based post combustion capture plant flue gas.

The method has been designed to measure nitrosoamine concentrations from about 5 ng/m^{3}n in (excluding NDELA which detection limit is 1 µg/m^{3}n) stationary source emissions.

Two different analytical methods are presented. Volatile (non-alcoholic) N-nitrosoamines are extracted with dichloromethane and determined by gas chromatography with mass spectrometer.

Less volatile (alcoholic) N-Nitrosamines are analysed by direct injection using UPLC-MS/MS due to the lack of reliable concentration step. N-nitrosodiethanolamine can also be analysed from solid absorption media such as fiber glass filters and Thermosorb-N cartridges.

Presented analytical methods are applicable for analysis of aqueous samples, samples collected on absorbtion media (such as Thermosorb-N cartridges) and amine based CCS-plant fluegas, washwater and absorption amine solutions. The concentration of solvent amines in matrix is tested up to 10 %.

Compounds of interest are presented in the Table 1.

Table 1 Scope of analytes

Compound	CAS number	Formula	Detection limit µg/m³n, sample volume 0,5 m3n
Volatile (non-alcoholic) Nitrosoamines			
N-nitrosodimethylamine (NDMA)	62-75-9	$C_2H_6N_2O$	0.005
N-nitrosodiethylamine (NDEA)	55-18-5	$C_4H_{10}N_2O$	0.005
N-nitrosomorpholine (NMOR)	59-89-2	$C_4H_8N_2O_2$	0.005
N-nitrosopiperidine (NPIP)	100-75-4	$C_5H_{10}N_2O$	0.005
N,N´-Dinitrosopiperazine (DNPIPA)	140-79-4	$C_4H_8N_4O_2$	0.005
Alcoholic N-nitrosoamine			
N-Nitrosodiethanolamine (NDELA)	1116-54-7	$C_4H_{10}N_2O_3$	1

3. NORMATIVE REFERENCES

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13284-1:2001, Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report

EN ISO 3696:1995, Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)

4. TERMS AND DEFINITIONS

4.1 Abbreviations

AMP	2-Amino-2-methyl-1-propanol
DCM	Dichloromethane
DEA	Diethanolamine
DEN	Diethylamine
DL	Detection Limit
DMA	Dimethylamine
DNPIPA	N,N´-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
IDL	Instrument Detection Limit
LMW	Low Molecular Weight
MDEA	N-Methyldiethanolamine
MDL	Method Detection Limit
MEA	Monoethanolamine
MeOH	Methanol, methyl alcohol
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
PCC	Post combustion CO_2-capture
RI	Refractive Index
SIM	Single-ion monitoring
SPE	Solid-Phase Extraction
T_b	Boiling point
TMA	Trimethylamine
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
vis	Visible

4.2 Terms and definitions

4.2.1 Solvent amine(s)
Common name used in this study for alkanolamines.

4.2.2 Isokinetic sampling
Sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as the velocity and direction of the gas in the duct at the sampling point.

4.2.3 Analytical blank value
Value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all relevant reagents and materials.

4.2.4 Limit of detection (LOD)
Minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability.
The measurement value can be distinguished from the analytical blank value with a confidence of 99%, when the limit of detection is expressed as the mean analytical blank value plus three times the standard deviation of the analytical blank.
The limit of detection should preferably be calculated from the analytical blank. If this is not possible, the limit of detection can be calculated from the signal to noise ratio.

4.2.5 limit of quantification (LOQ)
Limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus five to ten times the standard deviation of the analytical blank. The limit of quantification should preferably be calculated from the analytical blank. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio.

5. SAMPLING

5.1 Principle and minimum requirements

The test programme shall be established following the advice and requirements described in EN 15259:2007 (5.4, Clauses 6, 7 and 8).

Sampling should be carried out at one or several points in the sampling section, in accordance of the test of homogeneity carried out according the EN 15259.

Sampling is performed by using ambient temperature probe with a nozzle of know internal diameter, chilled condensate and absorption section, gas drying and sample gas volume measurements. A solid preservation chemical is added into condensate flask before sampling.

If sample gas will certainly not include drops, droplets or solid matter sampling may be performed as non-isokinetic sampling.

5.2 Side reactions during sampling

It is has been shown that some flue gas impurities (e.g. NO_x) reacts with some solvent and may affect the concentration of target compounds. Formed degradation products may give false rise of some impurities, e.g. nitrosamines. Also high temperatures in the sampling line may affect degradation. To avoid this, sulfamic acid is added into the condensate and absorbents flask.

5.3 Sampling train and its operations

Principle of the sampling train is presented at the Figure 1.

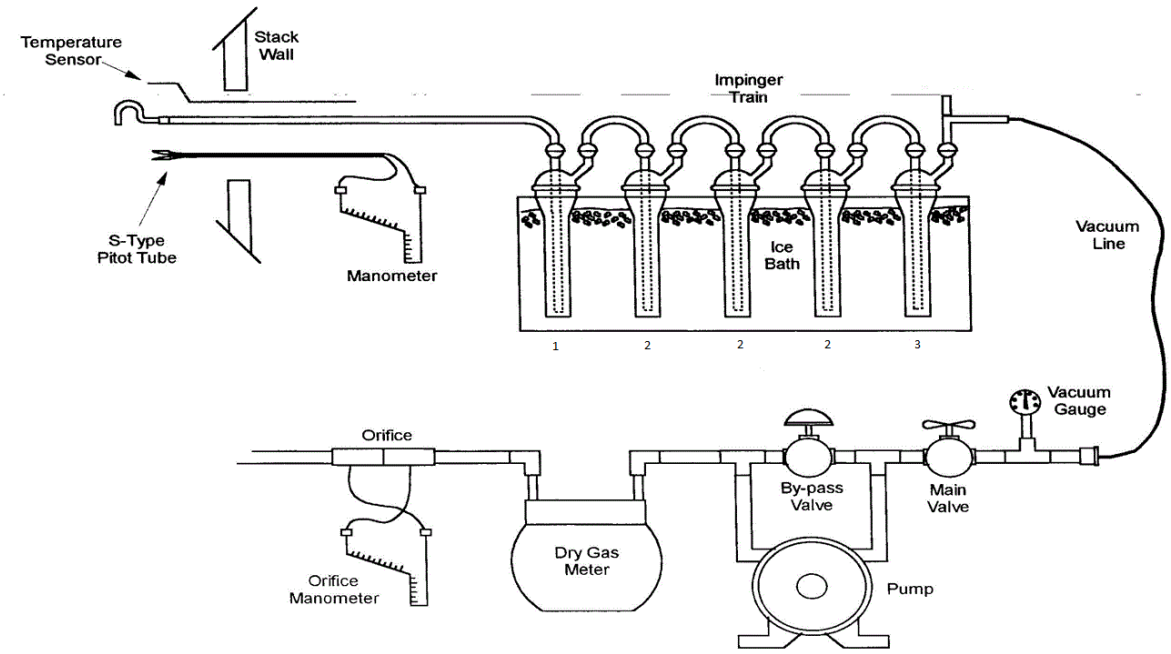


Figure 1. Principle of sampling arrangement, 1. condenser; 2. Absorbers; 3 silica gel

5.3.1 Probe

Unheated probe and entry nozzle without filter shall fulfil the requirements of EN 13284-1 excluding nozzle internal diameter which may be less than 6 mm. Nozzle i.d.'s less than 3.5 mm should be avoided. Area of nozzle entry should be specified in accuracy better than ±10 %.

Table 2 Evaluation of needed nozzle diameter at different flow gas velocities.

Nozzle size (diameter, mm)											
	sampling rate (l/min)										
Flow rate (m/s)	**0,2**	**0,5**	**1**	**2**	**4**	**6**	**8**	**10**	**12**	**16**	**20**
2	1,5	2,3	3,3	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	1,0	1,6	2,3	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	0,8	1,3	1,9	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	0,7	1,2	1,6	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	0,7	1,0	1,5	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	0,6	0,9	1,3	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	0,6	0,9	1,2	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	0,5	0,8	1,2	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	0,5	0,8	1,1	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	0,5	0,7	1,0	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

The probe should be about 0.5-1 meter longer than the diameter of duct. If two opposed sampling ports are available half of the duct diameter + 0.5- 1 m is adequate for the sampling probe

Accepted material of probe and nozzle is stainless steel (316 SS and 316l SS) or boron or quartz glass. Some minor parts as fitting and seals may be PTFE, otherwise it should be avoided. However, on very large ducts PTFE lines use may be necessary for the practical reasons, e.g. when moving the probe inside the duct. On that case internal volume of PTFE tube should be minimized and number of blanks and washing practises evaluated. Internal diameter and length of probe should be minimized.

The probe may be marked before sampling in order to reach more easily the representative measurement point(s) in the measurement plane. It is important to specify the direction of nozzle entry.

If sampling is performed from the highly negative pressure duct, back flush from the absorbers into the duct is possible before and after the sampling sequence when pump is stopped. To avoid

this, the connection between the probe and absorbers should be easily detached or suitable inert valve is recommended.

5.3.2 Condenser and absorber

To achieve an efficient absorption at least condenser and three absorbers shall be placed in series. Temperature of condensate flask and absorbers shall be cooled less that 5°C during the sampling.

On Condenser and absorbers the inner tube should reach the bottom of the impinger and end to bubble breaker or sintered frit to fine the bubbles.

Recommended size of impingers should be capable of sampling on isokinetic flow rates without significant overflow of absorbent liquids. Recommended size of impingers is about 500 ml/impinger and absorber liquid volume of 300 ml. Condensate flasks may be bigger especially in high humidity and a long sampling periods. Extra protection bottle is recommended before silica gel.

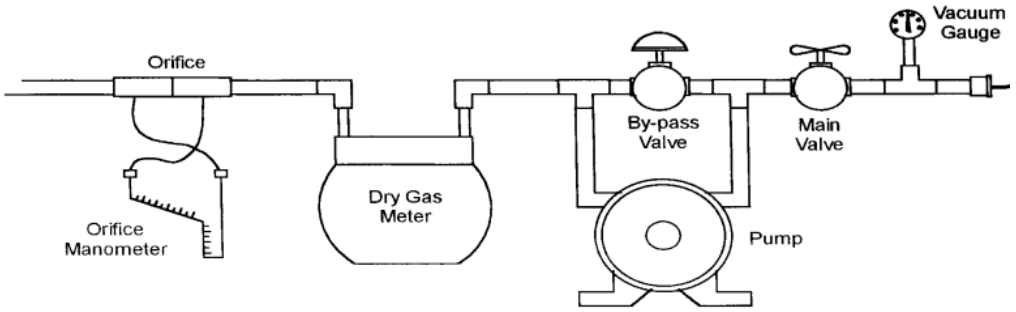
When sampling hot gas or at warm conditions, extra cooler may be needed before the condensate flask to avoid excessive break though of moisture from condensate flask into absorbers.

Absorption efficiency and carry out may be tested by analysing the last absorber separately. This may be hard to obtain for all analytes due to low concentration of analytes. In that case the analyte of highest concentration may be used for the evaluation, e.g. the main solvent amine. Breakthrough in the last bottle should not exceed 5 % from total amount.

Penetration of strong light into sampling system should be avoided because nitrosoamines degrade by light.

5.3.3 Sampling pump

Leak-free pump capable of sampling gas at a set flow rate.
NOTE. A rotameter (optional) facilitates the adjustment of the nominal sampling flow rate.



5.3.4 Gas volume meter

Dry or wet gas volume meter may be used providing the volume is measured with a relative uncertainty of calibration not exceeding 2 % at actual conditions. The gas volume-meter shall be equipped with a temperature measuring device (uncertainty of calibration less than 2.5 K). The absolute pressure at the gas volume meter (uncertainty of calibration less than 1.0 %) can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10.5 °C or a volume content $\chi(H2O)$ = 1.25 %).

For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at 110 °C for at least 2 h.
When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

The relative pressure can be neglected if the gas volume meter is the last equipment of the sampling chain.

5.3.5 Absorption reagents

Absorption liquid should be done in laboratory by diluting solid sulfamic acid into UHQ water. The concentration of absorption liquid is 0.1 M sulphamic acid (CAS 5329-14-6). Amount of 1 000 ml should be reserved for the one sample.

Solid sulfamic acid shall be added into condensate flask before sampling. The amount of sulfamic acid into condenser is 1000 mg/100 ml of expected amount of condensate. Small amount of water may be added into condensate flask before the sampling to dissolve sulfamic acid.

5.4 Sampling procedure

5.4.1 Preparation and installation of equipment

5.4.1.1 Sampling location and sampling points

The sampling location is chosen according to EN 15259. A grid measurement is performed if homogeneity of sample gas is not validated.

5.4.2 Sampling procedure

5.4.2.1 Preparation

Homogeneity in the sampling plane should be evaluated before sampling as well as development of flow (direction, turbulence). Size and the arrangement of the duct shall be measured and recorded.

Required space is reserved before the sampling. Ice bath shall be cooled before the sampling. Rinse the sampling system prior to sampling by UHQ water.

Fill the absorbers at the clean area. Proposed amount of absorbent in the impinger is 60 % of the total volume, e.g. at 500 ml impinger recommended absorbent volume is 300 ml.

5.4.2.2 Checks

Check the velocities of flow at the sampling points, and calculate the sampling parameters to be achieved at each point (volume flow rate, sampling time), if required.

Ensure that the sampling train has been correctly assembled, and is leak tight, performing leak tests before each sample. Leak test shall be performed as below:

a) Assemble the complete sampling system, including absorbers
b) Seal the nozzle, or if not practicable, a connection between the condensate flask and probe air tightly.
c) Switch on the pump
d) Observe the rotameter / gas meter. Leak shall not exceed 2 % of the expected gas flow rate.
e) Release the seal SLOWLY and let under pressure disappear from the sampling system BEFORE turning pump off to avoid back flush of absorbers. Fast release of under pressure may break the bottom of flat glass absorbers.
f) Turn off the pump

5.4.2.3 Field blank

This procedure is used to ensure that no significant contamination has occurred during all the steps of the measurement.

A field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this report. This includes the sampling procedure without the suction step.

If sampling system in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken before each measurement series. The blank taken after a measurement series may be used as the blank taken before the following measurement series.

The average sampling volume shall be used for calculation of the blank value expressed in µg/m^3n.

If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank.

Also sample from wash water, absorbent liquids and sulfamic acid used on measurement should be stored as blank samples. These will be analysed if field blank shows unexpected positive concentrations.

5.4.2.4 Sampling

Taking into account the expected concentration related to analytical detection limit and flue gas flow, calculate the required sample volume and time. Suggested sampling rate depends on the design of the absorption flasks. In practice sampling rate of 5-7 l/min and sampling time of 1-2 hours are applicable. Longer sampling times up to 6-8 hours may be required if lower concentrations at the level less than 1 ng/m³n are expected.

Sampling procedure is as follows:

a) Record the gas meter values, temperature, pressure, startup time
b) Insert the probe in the duct. If sampling will not start immediately turn the nozzle pointing to the downstream of the flow before the sampling
c) Turn on the sampling pump
d) On the conditions of strong negative pressure, connect the absorbers and the probe open the valve between
e) Adjust the sample flow to required value
f) On grid measurement move the probe and adjust the flow rate accordingly without stopping the pumps
g) Maintain the temperature of ice-bath at required level
h) At the end of sampling, turn off the pump. On ducts of strong negative pressure disconnect the probe and absorbents before stopping the pump. At the end of sampling record the final gas meter readings
i) Wash the probe by following procedure, if possible,:
    a. Take the probe out from the duct
    b. Turn on the sampling pump
    c. Add UHQ water into the nozzle (about 10 ml) using washing bottle
    d. Let the water run to the condenser and stop the pump. Pump values on washing are not included the total sample amount!
    e. If the probes are impractical to take out of the duct between the sampling periods, in the case of negative pressure in the duct, add clean UHQ water from the absorber end of the probe to wash the probe.
j) Pour the condensate into the storage vessel. Plastic vessels may be used if sample is immediately frozen. Other cases glass vials with inert and air tight cap shall be used.
k) Pour the absorbent solvents excluding the last absorbent into the storage vessel. NOTE! The condensate and absorption liquids are not combined. Last absorption vessel shall be stored at separate vessel.
l) Wash the condensate flask by UHQ water and pour the washing into the storage vessel of condensate. Wash the absorbers respectively.

5.4.2.5 Storage of samples

Samples should be stored in cold and dark. Frozen is recommended. Analysis should be performed as soon as possible.

6. SAMPLE PREPARATION

6.1 Principle

The determination of the nitrosoamines is based on quantification by deuterated internal standards using GC-HRMS or UPLC-MS. The deuterated internal standards are added to the sample before extraction. Losses during extraction, clean-up and concentration steps can be detected and compensated by using these deuterated compounds as internal standards for quantification. However, due to possible differences in the binding and adsorption characteristics between native and added deuterated compounds, complete substantiation of extraction

efficiency and compensation of possible losses is not guaranteed. Therefore the applied methods shall be validated thoroughly.
The high concentration of solvent amine(s) in the samples may interfere with the pretreatment and/or chromatographic separation. The maximum recommended solvent amine concentration is 5-10 % with the GC-method and 0,2 % with the UPLC-method.

6.2 Reagents and materials

6.2.1 Laboratory equipment

- Standard laboratory glassware such as separation funnels with tap and glass stopper, Erlenmeyer flasks and beakers
- Balances with appropriate range and precision
- Pipettes
- Vials for sample extracts
- Millipore MilliQ water cleaning system
- TurboVap -automated solvent evaporation system

6.2.2 Reagents

Solvents and reagents of sufficient purity shall be used, for example

- Dichloromethane (J.T. Baker (high purity) or equivalent)
- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- Anhydrous $NaSO_4$ (J.T. Baker (high purity) or equivalent)
- Hydrochloric acid (J.T. Baker (high purity) or equivalent)
- Formic acid (J.T. Baker (98 %) or equivalent)
- Acetonitrile (BDH Prolabo (LC-MS grade) or equivalent)
- Isopropanol (J.T. Baker (HPLC-grade) or equivalent)

6.2.3 Standards

High purity standards shall be used, for example

- N-Nitrosodimethylamine (Accustandard, Inc.), purity 100%
- N-Nitrosodiethylamine (Chem Service, Inc.), purity 99.5 %
- N-Nitrosomorpholine (Chem Service, Inc.), purity 99.5 %
- N-Nitrosopiperidine (Chem Service, Inc.), purity 99.0 %
- N,N´-Dinitrosopiperazine (Chemos GmbH), purity 99.0 %
- N-Nitrosodiethanolamine (Chem Service, Inc.), purity 99.5 %

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

6.2.4 Internal standards (ISTD)

High purity standards shall be used, for example

- N-Nitrosodimethyl-D_6-amine (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %
- N-Nitrosomorpholine-D_8 (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %
- 1,4-Dinitrosopiperazine-D_8 (Chiron AS), Purity 95%, Deuteration degree 98.6 %
- N-Nitrosopiperidine-D_{10} (Chiron AS), Purity 99.8%, Deuteration degree 99.2 %
- N-Nitrosodiethylamine-D_{10} (Chiron AS), Purity 99%, Deuteration degree 99.4 %
- N-nitrosodiethanolamine-D8 (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

6.3 Procedure, gas chromatographic method

Sample spiked with mass-labeled internal standards is extracted with dichloromethane prior to analysis with GC-HRMS –apparatus.

6.3.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.3.2 Quality control

Standard addition to the sample matrix will be done with each sample set. Recoveries will be monitored.

6.3.3 Pretreatment and cleaning

Aqueous samples
If the whole sample is planned to be analyzed the container must be weighed before and after extraction. Otherwise a subsample of known volume is taken. Internal standards (for example 50 µL of 10 mg/L solution) are added to the sample.
When possible, a spiked (standard addition at desired level) sample is done to the sample matrix. Otherwise spiked sample will be done to UHQ-water which is adjusted to similar solvent amine concentration with the samples (synthetic matrix).
Samples (including standards and quality controls) are extracted twice with dichloromethane using total of 50mL solvent. The volume can be adjusted according to the sample volume as long as sufficient extraction efficiency is achieved.
When high solvent amine concentration is expected, the combined extracts are washed-up with 50 ml of 1M HCl- solution.
The cleaned extracts are dried with anhydrous $NaSO_4$ and evaporated by TurboVap to volume of 0.5 ml. Finally the samples are transferred to GC vials and analyzed.

Other media:
Thermosorb-N samples are spiked with labeled internal standards and desorbed with 75/25 (v/v) dichloromethane/methanol solution. The sample is eluted by gently forcing the desorption solvent through the air sampler at approximately 0.5 ml/min.
To the collected 2 ml of extract 1 ml of 0,1 M HCl-solution is added. After shaking, the dichloromethane layer is collected and transferred to GC vials for analysis.

6.4 Procedure, liquid chromatographic method

An aliquot of aqueous sample (e.g. condensate from flue gas sampling) is injected to analysis vial and diluted with methanol to final consistency of 10 % methanol and analysed with UPLC-MS/MS.

6.4.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.4.2 Quality control

Standard addition to the sample matrix will be done with each sample set. Recoveries will be monitored.

6.4.3 Pretreatment and cleaning

Aqueous samples
The total sample volume shall be measured with a suitable analytical balance. An aliquot of 900 µL is injected to vial, internal standards (in methanol) are added e.g. 50 µL of 2 mg/L solution and methanol is added to final volume of 1000 µL. If precipitation is observed the sample is filtered thru an disposable syringe filter (0,2 µm) and analysed.

Fiber glass filter samples
Filter is placed into a suitable test tube and immersed into 5 mL of isopropanol. Also blank filter and spiked filter is placed into identical test tubes and pretreated the same way. Internal standard e.g. 50 µL of 2 mg/L is added and the test tubes are shaked in a test tube shaker for no less than 60 minutes. The solvent is filtered together with the filter remnants with disposable syringe and syringe filter (0,2 µm). The filtrate is then evaporated to final volume of 500 µL, transferred to LC vial and analysed.

Thermosorb-N cartridge
The water/methanol washing solution from chapter 6.3.3 is evaporated in TurboVap extraction workstation in to final volume of 500 µL and 400 µL of UHQ water and 50 µL of methanol is added, placed in a vial and analysed.

7. INSTRUMENTAL ANALYSIS, GC-METHOD

7.1 Instruments and chemicals

GC with high resolution mass spectrometry detection is preferred. Some studied nitrosoamines have very simple mass spectra and lack useful qualifier ions. The use of higher resolving power offers better selectivity.
GC-system should offer baseline separation of all the nitrosoamines to be analyzed. The volatile nitrosoamines chromatograph quite well on different columns. Conditions as followed have been tested:

- Column: Restek Rtx-Dioxin2 (40m, 0.25 mm, i.d. 0,18 µm film)
- Carrier Gas: helium at constant flow of 1.2 ml/min.
- Injection: splitless injection 200°C, injection volume 1 µL.
- Oven program: 30°C hold 5min, 10°C/min to 120°C, 5°C/min to140°C, 10°C/min to 220°C and 30°C/min to 320°C hold 5 min (postrun).

Ion source (EI)

- Temp 260°C
- Electron energy: 35 eV
- Trap current: 650 µA

7.2 Calibration

7.2.1 Calibration references

Standard solutions will be done at 10 mg/l concentration in methanol.
External standards are diluted to the range of 10-500 µg/L. Calibration should be carried out with at least four calibration solutions. These solutions contain all native and deuterated nitrosoamine standards in precisely defined amounts.

7.3 Procedure

Analysis of samples is done with GC-HRMS system. Minimum recommended resolution of mass spectrometry is 5000 (5% peak height). The monitored masses are presented in the table below.

Table 2. Monitored masses

Compound	m/z of analytes	m/z of perfluorokerosene reference peaks (lock mass)
N-Nitrosodimethylamine (NDMA)	74.0480	92.9952 or 99.9936
N-Nitrosodimethylamine-D_6	80.0851	
N-Nitrosodiethylamine (NDEA)	102.0793	99.9936
N-Nitrosodiethylamine-D_{10}	112.1411	
N-Nitrosomorpholine (NMOR)	86.0606 (and/or 116.0586)	92.9952 or 99.9936
N-Nitrosomorpholine-D_8	94.1100 (and/or 124.1080)	
N-Nitrosopiperidine (NPIP)	114.0793	99.9936
N-Nitrosopiperidine-D_{10}	124.1411	
1,4-Dinitrosopiperazine (DNPIPA)	84.0687 (and/or 114.0668)	92.9952 or 99.9936
1,4-Dinitrosopiperazine-D_8	92.1182 (and/or 122.1162)	

7.3.1 Calculation of results

Results are calculated using deuterated internal standards for quantification. Final results will be given in units corresponding to concentration of sample.

7.3.2 Uncertainty

The recoveries vary within and between batches and from compound to compound. Therefore deuterated nitrosoamines structurally similar to analytes are used as internal standards. The recoveries should be monitored and results should be carefully evaluated if recoveries fall outside normal levels. Addition of an extra deuterated nitrosoamine to act as a recovery standard is recommended to allow the recoveries to be calculated more accurately.
Blanks may contain nitrosoamines and LOD ja LOQ values should be calculated using mean analytical blank values rather than signal to noise ratio.
To avoid artifactual formation of nitrosoamines, samples should be freezed if need to be storaged longer periods. Preferably sample storage times are kept to minimum.

7.4 Quality assurance

Recoveries of internal standards and the recoveries of standard additions and blank values are monitored.

8. INSTRUMENTAL ANALYSIS, LC-METHOD

8.1 Instruments and chemicals

UPLC with tandem mass spectrometer is used in all analysis of NDELA. Chromatographically NDELA will not separate from ethanolamine with reversed phase columns. First signs of signal suppression will start when MEA concentration exceeds 0.2 % in the vial.

The UPLC conditions are as followed:

- Column Phenomenex kinetex C18 with guard column (100 x 2.1 mm, 2.6 µm)
- Column temperature 40 ºC
- Eluents 0.02 % HCOOH in UHQ (A) and 0.02 % HCOOH in methanol (B)
- Injection volume 5 µL
- Gradient 95/5 (A%/B%) for 3 min, 50/50 at 6 min, 10/90 at 8 min, 95/5 at 10 min. Total run time 12 min

Applicable start point for the settings in ion source are (Waters Xevo):

Ionisation	Electro spray ionisation (ESI)	
Source temp	150	ºC
Desolvation temp	400	ºC
Capillary voltage	3,6	kV
Desolvation flow	800	L/h
Cone flow	50	L/h

8.2 Calibration

8.2.1 Calibration references

Standard solutions will be done at 10 mg/l concentration in methanol.
External standards are diluted to the range of 1-500 µg/L. Calibration should be carried out with at least four calibration solutions. These solutions contain all native and deuterated nitrosoamine standards in precisely defined amounts.

8.3 Procedure

Analysis of samples is done with UPLC-MS/MS system and minimum of two transitions is monitored:

- NDELA 135.10 → 103.98 and 135.10 → 73.86
- NDELA D8 143.16 → 110.9661 and 143.16 → 79.935

8.3.1 Calculation of results

Results are calculated using deuterated internal standard for quantification. Final results will be given in units corresponding to concentration of sample.

8.3.2 Uncertainty

The recovery with filter and solid absorbent samples tend to have some variance, therefore deuterated nitrosoamines structurally similar to analytes are used as internal standards. The recoveries should be monitored and results should be carefully evaluated if recoveries fall outside normal levels. Addition of an extra deuterated nitrosoamine to act as a recovery standard is recommended to allow the recoveries to be calculated more accurately.
Blanks may contain nitrosoamines and so LOD and LOQ values should be calculated using mean analytical blank values rather than signal to noise ratio.
To avoid formation of nitrosoamines, samples should be frozen if need to be storage longer periods. Preferably sample storage times are kept to minimum.

8.4 Quality assurance

Recoveries of internal standards and the recoveries of standard additions and blank values are monitored.

9. RESULTS

9.1 Calculations

Results are calculated using deuterated internal standards for quantification. Final results will be given in units corresponding to concentration of sample.

9.1.1 Sample amount

$$Q_{analyte} = C \times V_s$$

$Q_{analyte}$	quantity of nitrosoamines collected, in micrograms;
C	is the concentration of the solution in micrograms per millilitre;
V_s	is the volume of absorption solution in millilitres

9.1.2 Sample gas volume

For dry gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_{res}}{101{,}3}$$

For wet gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_s(H_2O)}{101{,}3}$$

Where

V_{std}	the volume under standard conditions and dry basis, in cubic metres (m^3)
V_{Tp}	the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m^3);
T	Actual temperature in Kelvins
p	Total pressure in kPa at the gas meter
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);
P_{res}	is the residual vapour pressure, in kilopascals (kPa).

9.1.3 Final concentration

Final concentration in the flue gas is expressed as:

$$C_{analyte}\ [\mu g/m^3 n] = \frac{Q_{analyte}}{V_{std}}$$

9.2 Overall method uncertainty

For volatile nitrosamines the tested analytical repeatability (RSD%) was < 2%. Tested accuracy for all nitrosoamines was less than ±10 %.

Estimation of overall uncertainty including sampling is ±30 - 40 %.

APPENDIX 2
SAMPLING AND ANALYSIS OF SOLVENT AMINES

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1. INTRODUCTION

This report presents the current sampling and analysis methods developed by Ramboll Analytics for solvent amines emitting from the ducts and stacks. Methods may also be applied for the analysis of wash water and solvent in amine based post combustion capture processes (PCC).

2. SCOPE

The proposed method specifies the sampling, extraction and analysis procedures of the studied solvent amines in monoethanolamine (MEA) based CCS-plant flue gas.

The method has been designed to measure solvent amines concentrations from stationary source emissions as follows, sample amount 500 liters:

Method is also applicable for the sampling of volatile and non-volatile nitrosoamines and probably sampling of nitramines.

The analysis of solvent amines is performed by direct injection to UPLC-MS/MS. The analytical methods proposed are applicable for analysis of aqueous samples, and amine based CCS-plant flue gas, wash water and absorption amine solutions.

Scope of analytes is presented on the table 1.

Table 1 Scope of analytes

Compound	**CAS-number**	**Max. MEA concentration the liquid sample**	**Detection limit µg/m³n, sample volume 0,5 m³n**
2-amino-2-methyl-1-propanol (AMP)	124-68-5	0,2 %*	1
Diethanolamine (DEA)	111-42-2	0,2 %*	3
1,2-diaminoethane (EDA)	107-15-3	0,2 %*	50
N-methyldiethanol-amine (MDEA)	105-59-9	0,2 %*	10
Monoethanolamine (MEA)	141-43-5	100 %	1
Piperazine	110-85-0	not evaluated	not evaluated

** Instrumental response for piperazine is weak when compared to other compounds*

3. NORMATIVE REFERENCES

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13284-1:2001, Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report

EN ISO 3696:1995, Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)

4. TERMS AND DEFINITIONS

4.1 Abbreviations

AMP	2-Amino-2-methyl-1-propanol
DCM	Dichloromethane
DEA	Diethanolamine
DEN	Diethylamine
DL	Detection Limit

DMA	Dimethylamine
DNPIPA	N,N´-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
IDL	Instrument Detection Limit
LMW	Low Molecular Weight
MDEA	N-Methyldiethanolamine
MDL	Method Detection Limit
MEA	Monoethanolamine
MeOH	Methanol, methyl alcohol
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
PCC	Post combustion CO_2-capture
RI	Refractive Index
SIM	Single-ion monitoring
SPE	Solid-Phase Extraction
T_b	Boiling point
TMA	Trimethylamine
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
vis	Visible

4.2 Terms and definitions

4.2.1 Solvent amine(s)
Common name used in this study for alkanolamines.

4.2.2 Isokinetic sampling
Sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as the velocity and direction of the gas in the duct at the sampling point.

4.2.3 Analytical blank value
Value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all relevant reagents and materials.

4.2.4 Limit of detection (LOD)
Minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability.
The measurement value can be distinguished from the analytical blank value with a confidence of 99%, when the limit of detection is expressed as the mean analytical blank value plus three times the standard deviation of the analytical blank.
The limit of detection should preferably be calculated from the analytical blank. If this is not possible, the limit of detection can be calculated from the signal to noise ratio.

4.2.5 Limit of quantification (LOQ)
Limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus five to ten times the standard deviation of the analytical blank. The limit of quantification should preferably be calculated from the analytical blank. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio.

5. SAMPLING

5.1 Principle and minimum requirements

The test programme shall be established following the advice and requirements described in EN 15259:2007 (5.4, Clauses 6, 7 and 8).

Sampling should be carried out at one or several points in the sampling section, in accordance of the test of homogeneity carried out according the EN 15259.

Sampling is performed by using ambient temperature probe with a nozzle of know internal diameter, chilled condensate and absorption section, gas drying and sample gas volume measurements. A solid preservation chemical is added into condensate flask before sampling.

If sample gas will certainly not include drops, droplets or solid matter sampling may be performed as non-isokinetic sampling.

5.2 Side reactions during sampling

It is has been shown that some flue gas impurities (e.g. NO_x) reacts with some solvent and may affect the concentration of target compounds. Formed degradation products may give false rise of some impurities, e.g. nitrosamines. Also high temperatures in the sampling line may affect degradation. To avoid this, sulfamic acid is added into the condensate and absorbents flask.

5.3 Sampling train and its operations

Principle of the sampling train is presented at the Figure 1.

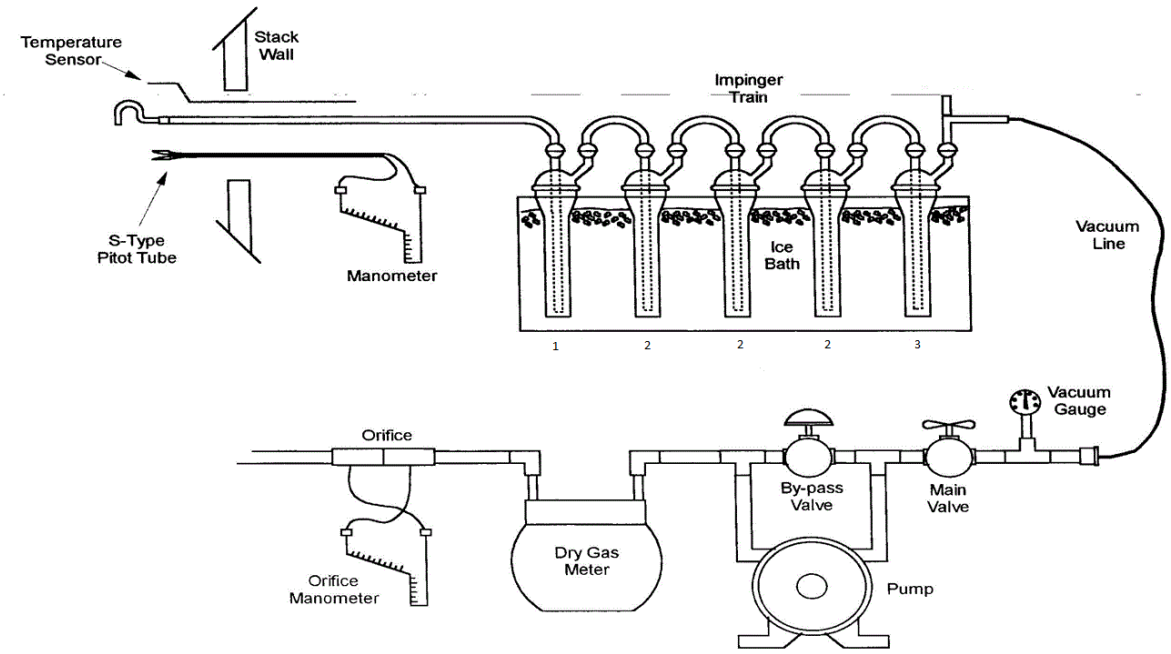


Figure 1. Principle of sampling arrangement, 1. condenser; 2. Absorbers; 3 silica gel

5.3.1 Probe

Unheated probe and entry nozzle without filter shall fulfil the requirements of EN 13284-1 excluding nozzle internal diameter which may be less than 6 mm. Nozzle i.d.'s less than 3.5 mm should be avoided. Area of nozzle entry should be specified in accuracy better than ±10 %.

Table 2 Evaluation of needed nozzle diameter at different flow gas velocities.

Nozzle size (diameter, mm)											
	sampling rate (l/min)										
Flow rate (m/s)	**0,2**	**0,5**	**1**	**2**	**4**	**6**	**8**	**10**	**12**	**16**	**20**
2	1,5	2,3	3,3	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	1,0	1,6	2,3	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	0,8	1,3	1,9	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	0,7	1,2	1,6	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	0,7	1,0	1,5	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	0,6	0,9	1,3	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	0,6	0,9	1,2	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	0,5	0,8	1,2	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	0,5	0,8	1,1	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	0,5	0,7	1,0	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

The probe should be about 0.5-1 meter longer than the diameter of duct. If two opposed sampling ports are available half of the duct diameter + 0.5- 1 m is adequate for the sampling probe

Accepted material of probe and nozzle is stainless steel (316 SS and 316l SS) or boron or quartz glass. Some minor parts as fitting and seals may be PTFE, otherwise it should be avoided. However, on very large ducts PTFE lines use may be necessary for the practical reasons, e.g. when moving the probe inside the duct. On that case internal volume of PTFE tube should be minimized and number of blanks and washing practises evaluated. Internal diameter and length of probe should be minimized.

The probe may be marked before sampling in order to reach more easily the representative measurement point(s) in the measurement plane. It is important to specify the direction of nozzle entry.

If sampling is performed from the highly negative pressure duct, back flush from the absorbers into the duct is possible before and after the sampling sequence when pump is stopped. To avoid

this, the connection between the probe and absorbers should be easily detached or suitable inert valve is recommended.

5.3.2 Condenser and absorber

To achieve an efficient absorption at least condenser and three absorbers shall be placed in series. Temperature of condensate flask and absorbers shall be cooled less that 5°C during the sampling.

On Condenser and absorbers the inner tube should reach the bottom of the impinger and end to bubble breaker or sintered frit to fine the bubbles.

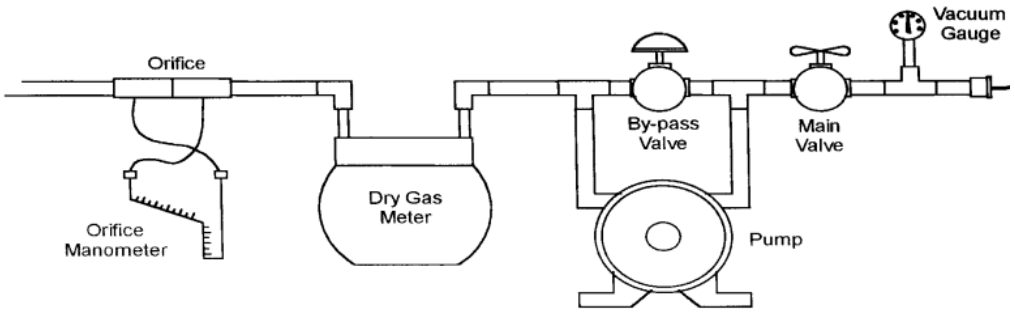
Recommended size of impingers should be capable of sampling on isokinetic flow rates without significant overflow of absorbent liquids. Recommended size of impingers is about 500 ml/impinger and absorber liquid volume of 300 ml. Condensate flasks may be bigger especially in high humidity and a long sampling periods. Extra protection bottle is recommended before silica gel.

When sampling hot gas or at warm conditions, extra cooler may be added before the condensate flask to avoid excessive break though of moisture from condensate flask into absorbers.

Absorption efficiency and carry out may be tested by analysing the last absorber separately. This may be hard to obtain for all analytes due to low concentration of analytes. In that case the analyte of highest concentration may be used for the evaluation, e.g. the main solvent amine. Breakthrough in the last bottle should not exceed 5 % from total amount.

5.3.3 Sampling pump

Leak-free pump capable of sampling gas at a set flow rate.
NOTE. A rotameter (optional) facilitates the adjustment of the nominal sampling flow rate.



5.3.4 Gas volume meter

Dry or wet gas volume meter may be used providing the volume is measured with a relative uncertainty of calibration not exceeding 2 % at actual conditions. The gas volume-meter shall be equipped with a temperature measuring device (uncertainty of calibration less than 2.5 K). The absolute pressure at the gas volume meter (uncertainty of calibration less than 1.0 %) can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10.5 °C or a volume content $\chi(H2O)$ = 1.25 %).

For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at 110 °C for at least 2 h.
When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

The relative pressure can be neglected if the gas volume meter is the last equipment of the sampling chain.

5.3.5 Absorption reagents

Absorption liquid should be done in laboratory by diluting solid sulfamic acid into UHQ water. The concentration of absorption liquid is 0.1 M sulphamic acid (CAS 5329-14-6). Amount of 1 000 ml should be reserved for the one sample.

Solid sulfamic acid shall be added into condensate flask before sampling. The amount of sulfamic acid into condenser is 1000 mg/100 ml of expected amount of condensate. Small amount of water may be added into condensate flask before the sampling to dissolve sulfamic acid.

5.4 Sampling procedure

5.4.1 Preparation and installation of equipment

5.4.1.1 Sampling location and sampling points

The sampling location is chosen according to EN 15259. A grid measurement is performed if homogeneity of sample gas is not validated.

5.4.2 Sampling procedure

5.4.2.1 Preparation

Homogeneity in the sampling plane should be evaluated before sampling as well as development of flow (direction, turbulence). Size and the arrangement of the duct shall be measured and recorded.

Required space is reserved before the sampling. Ice bath shall be cooled before the sampling. Rinse the sampling system prior to sampling by UHQ water.

Fill the absorbers at the clean area. Proposed amount of absorbent in the impinger is 60 % of the total volume, e.g. at 500 ml impinger recommended absorbent volume is 300 ml.

5.4.2.2 Checks

Check the velocities of flow at the sampling points, and calculate the sampling parameters to be achieved at each point (volume flow rate, sampling time), if required.

Ensure that the sampling train has been correctly assembled, and is leak tight, performing leak tests before each sample. Leak test shall be performed as below:

a) Assemble the complete sampling system, including absorbers
b) Seal the nozzle, or if not practicable, a connection between the condensate flask and probe air tightly.
c) Switch on the pump
d) Observe the rotameter / gas meter. Leak shall not exceed 2 % of the expected gas flow rate.
e) Release the seal SLOWLY and let under pressure disappear from the sampling system BEFORE turning pump off to avoid back flush of absorbers. Fast release of under pressure may break the bottom of flat glass absorbers.
f) Turn off the pump

5.4.2.3 Field blank

This procedure is used to ensure that no significant contamination has occurred during all the steps of the measurement.

A field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this report. This includes the sampling procedure without the suction step.

If sampling system in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken before each measurement series. The blank taken after a measurement series may be used as the blank taken before the following measurement series.

The average sampling volume shall be used for calculation of the blank value expressed in $\mu g/m^3n$.

If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank.

Also sample from wash water, absorbent liquids and sulfamic acid used on measurement should be stored as blank samples. These will be analysed if field blank shows unexpected positive concentrations.

5.4.2.4 Sampling

Taking into account the expected concentration related to analytical detection limit and flue gas flow, calculate the required sample volume and time. Suggested sampling rate depends on the design of the absorption flasks. In practice sampling rate of 5-7 l/min and sampling time of 1-2 hours are applicable. Longer sampling times up to 6-8 hours may be required if lower concentrations at the level less than 1 $\mu g/m^3n$ are expected and concentration step is not available on the analysis step.

Sampling procedure is as follows:

a) Record the gas meter values, temperature, pressure, startup time
b) Insert the probe in the duct. If sampling will not start immediately turn the nozzle pointing to the downstream of the flow before the sampling
c) Turn on the sampling pump
d) On the conditions of strong negative pressure, connect the absorbers and the probe open the valve between
e) Adjust the sample flow to required value
f) On grid measurement move the probe and adjust the flow rate accordingly without stopping the pumps
g) Maintain the temperature of ice-bath at required level
h) At the end of sampling, turn off the pump. On ducts of strong negative pressure disconnect the probe and absorbents before stopping the pump. At the end of sampling record the final gas meter readings
i) Wash the probe by following procedure, if possible,:
    a. Take the probe out from the duct
    b. Turn on the sampling pump
    c. Add UHQ water into the nozzle (about 10 ml) using washing bottle
    d. Let the water run to the condenser and stop the pump. Pump values on washing are not included the total sample amount!
    e. If the probes are impractical to take out of the duct between the sampling periods, in the case of negative pressure in the duct, add clean UHQ water from the absorber end of the probe to wash the probe.
j) Pour the condensate into the storage vessel. Plastic vessels may be used if sample is immediately frozen. Other cases glass vials with inert and air tight cap shall be used.
k) Pour the absorbent solvents excluding the last absorbent into the storage vessel. NOTE! The condensate and absorption liquids are not combined. Last absorption vessel shall be stored at separate vessel.
l) Wash the condensate flask by UHQ water and pour the washing into the storage vessel of condensate. Wash the absorbers respectively.

5.4.2.5 Storage of samples

Samples should be stored in cold. Frozen is recommended. Analysis should be performed as soon as possible.

6. SAMPLE PREPARATION

6.1 Principle

The determination of the solvent amines is based on direct injections UPLC-MS/MS. The sample is typically diluted with several steps and analysed and quantified against external standard curve.

6.2 Reagents and materials

6.2.1 Laboratory equipment

- Standard laboratory glassware such as Erlenmeyer flasks and beakers
- Balances with appropriate range and precision
- Pipettes
- Vials for sample extracts
- Millipore MilliQ water cleaning system

6.2.2 Reagents

Solvents and reagents of sufficient purity shall be used, for example

- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- Formic acid (J.T. Baker (98 %) or equivalent)
- Acetonitrile (BDH Prolabo (LC-MS grade) or equivalent)
- UHQ water (Millipore or equivalent)

6.2.3 Standards

High purity standards shall be used, for example

- Diethanolamine (Chem Service Inc. O-305) purity 99,5 %
- Ethanolamine (Chem Service Inc. O-311) purity 99,5 %
- 2-Amino-2-methyl-1-propanol (Chem Service Inc. O-301) purity 99,5 %
- Piperazine (Chem Service Inc. O-331), Purity 99,5 %
- N-methyldiethanol-amine (Merck) purity >98 %

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

6.2.4 Internal standards (ISTD)

None

6.3 Procedure, aqueous samples and flue gas samples

An aliquot of sample is diluted with several steps and dilutions with different ratios are analysed with UPLC-MS/MS.

6.3.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.3.2 Quality control

Standard addition to the sample matrix will be done with each sample set. Recoveries will be monitored.

6.3.3 Pretreatment and cleaning

Aqueous samples

The total sample volume shall be measured with a suitable analytical balance. Dilution should be done with multiple steps assuring adequate mixing of every step. Typical dilution factors for wash water are 1/1000000 and 1/100000, for flue gas condensate 1/1000 and 1/100 and for absorption solutions 1/100 and 1/10.

A spiked (standard addition at desired level) sample is done to the diluted sample matrix.

7. INSTRUMENTAL ANALYSIS

7.1 Instruments and chemicals

UPLC-MS/MS apparatus is used in all analyses and a minimum of two transitions per analyte is monitored (when possible). Chromatographically complete separation of analytes is challenging and it is likely that some overlapping will occur. The UPLC conditions are identical to the ones with alkylamines and are as followed:

- Column Supelco Discovery® HS F5 (150 x 2,1 mm, 3 µm)
- Column temperature 40 ºC
- Eluents 0,02 % HCOOH in UHQ (A) and 0,02 % HCOOH in acetonitrile (B)
- Injection volume 5 µL
- Gradient 95/5 (A%/B%) for 5 min, 75/25 at 6 min, 30/70 at 12 min, 10/90 at 13 min and 95/5 at 14 min. Total run time 15 min

Applicable start points for the settings in ion source are (Waters Xevo):

Ionisation	Electro spray ionisation (ESI)	
Source temp	150	ºC
Desolvation temp	600	ºC
Capillary voltage	0,5	kV
Desolvation flow	1000	L/h
Cone flow	50	L/h

7.2 Calibration

Calibration references
Standard solutions will be done at 10 mg/l concentration in methanol.
External standards are diluted to the range of 10-1000 µg/L. Calibration should be carried out with at least four calibration solutions.

7.3 Procedure

Analysis of samples is done with UPLC-MS/MS system and minimum of two transitions is monitored (excluding MEA):

- Monoethanolamine: 62,085 → 43,972
- Diethanolamine: 106,16 → 69,925 and 106,16 → 87,933
- Methyldiethanolamine: 120,196 → 57,914 and 120,196 → 101,945
- 2-Amino-2-methyl-1-propanol: 90,132 → 72,912 and 90,132 → 54,912
- Piperazine: 87,132 → 43,95 and 87,132 → 69,909

7.4 Limit of quantification

Limit of quantification is dependent of the sample matrix and is generally between 5 and 10 µg/L given as concentration of the LC vial.

7.5 Quality assurance

Recoveries of standard additions and blank values are monitored.

8. RESULTS

8.1 Calculations

Analysis results are calculated with TargetLynx software using quantification method for solvent amines. Final results will be given in units corresponding to concentration of sample.

8.1.1 Sample amount

$$Q_{analyte} = C \times V_s$$

$Q_{analyte}$	quantity of amine collected, in micrograms;
C	is the concentration of the solution in micrograms per millilitre;
V_s	is the volume of absorption solution in millilitres

8.1.2 Sample gas volume

For dry gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_{res}}{101{,}3}$$

For wet gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_s(H_2O)}{101{,}3}$$

Where

V_{std}	the volume under standard conditions and dry basis, in cubic metres (m^3)
V_{Tp}	the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m^3);
T	Actual temperature in Kelvins
p	Total pressure in kPa at the gas meter
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);
P_{res}	is the residual vapour pressure, in kilopascals (kPa).

8.1.3 Final concentration

Final concentration in the flue gas is expressed as:

$$C_{analyte}\ [\mu g/m^3 n] = \frac{Q_{analyte}}{V_{std}}$$

8.2 Method uncertainty

During the method development tested analytical accuracy for MEA was ±28 %.

APPENDIX 3
SAMPLING AND ANALYSIS OF ALKYL AMINES

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1. INTRODUCTION

This report presents the current sampling and analysis methods developed by Ramboll Analytics for alkyl amines emitting from the ducts and stacks. Methods may also be applied for the analysis of wash water and solvent in amine based post combustion capture processes (PCC).

2. SCOPE

The proposed method specifies the sampling, extraction and analysis procedures of the studied alkylamines in monoethanolamine (MEA) based CCS-plant flue gas, wash water and solvent amine.

The method has been designed to measure alkylamine concentrations from and above 5 µg/m^{3}n in stationary source emissions.

The analysis of alkylamines is performed by direct injection to UPLC-MS/MS. The analytical method proposed is applicable for analysis of aqueous samples and amine based CCS-plant flue gas, wash water and absorption solutions.

Table 1. Scope of analytes

Compound	**CAS-number**	**Max. MEA concentration the liquid sample**	**Detection limit µg/m³n, sample volume 0,5 m³n**
Diethylamine (DEN)	109-89-7	0.2 %*	1
Dimethylamine (DMA)	124-40-3	0.2 %*	1
Ethylamine (EA)	75-04-7	0.2 %*	1
Methylamine (MMA)	74-89-5	0.2 %*	1
Triethylamine (TEA)	121-44-8	0.2 %*	1
Trimethylamine (TMA)	75-50-3	0.2 %*	1

**max. concentration not evaluated*

3. NORMATIVE REFERENCES

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13284-1:2001, Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report

EN ISO 3696:1995, Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)

4. TERMS AND DEFINITIONS

4.1 Abbreviations

AMP	2-Amino-2-methyl-1-propanol
DCM	Dichloromethane
DEA	Diethanolamine
DEN	Diethylamine
DL	Detection Limit
DMA	Dimethylamine
DNPIPA	N,N´-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
IDL	Instrument Detection Limit
LMW	Low Molecular Weight
MDEA	N-Methyldiethanolamine
MDL	Method Detection Limit
MEA	Monoethanolamine
MeOH	Methanol, methyl alcohol
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
PCC	Post combustion CO_2-capture
RI	Refractive Index
SIM	Single-ion monitoring
SPE	Solid-Phase Extraction
T_b	Boiling point
TMA	Trimethylamine
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
vis	Visible

4.2 Terms and definitions

4.2.1 Solvent amine(s)

Common name used in this study for alkanolamines.

4.2.2 Isokinetic sampling

Sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as the velocity and direction of the gas in the duct at the sampling point.

4.2.3 Analytical blank value

Value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all relevant reagents and materials.

4.2.4 Limit of detection (LOD)

Minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability.

The measurement value can be distinguished from the analytical blank value with a confidence of 99%, when the limit of detection is expressed as the mean analytical blank value plus three times the standard deviation of the analytical blank.
The limit of detection should preferably be calculated from the analytical blank. If this is not possible, the limit of detection can be calculated from the signal to noise ratio.

4.2.5 Limit of quantification (LOQ)
Limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus five to ten times the standard deviation of the analytical blank. The limit of quantification should preferably be calculated from the analytical blank. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio.

5. SAMPLING

5.1 Principle and minimum requirements

The test programme shall be established following the advice and requirements described in EN 15259:2007 (5.4, Clauses 6, 7 and 8).

Sampling should be carried out at one or several points in the sampling section, in accordance of the test of homogeneity carried out according the EN 15259.

Sampling is performed by using ambient temperature probe with a nozzle of know internal diameter, chilled condensate and absorption section, gas drying and sample gas volume measurements. A solid preservation chemical is added into condensate flask before sampling.

If sample gas will certainly not include drops, droplets or solid matter sampling may be performed as non-isokinetic sampling.

5.2 Side reactions during sampling

It is has been shown that some flue gas impurities (e.g. NO_x) reacts with some solvent and may affect the concentration of target compounds. Formed degradation products may give false rise of some impurities, e.g. nitrosamines. Also high temperatures in the sampling line may affect degradation. To avoid this, sulfamic acid is added into the condensate and absorbents flask. Alkylamines are volatile which shall be taken in account when handling the samples.

5.3 Sampling train and its operations

Principle of the sampling train is presented at the Figure 1.

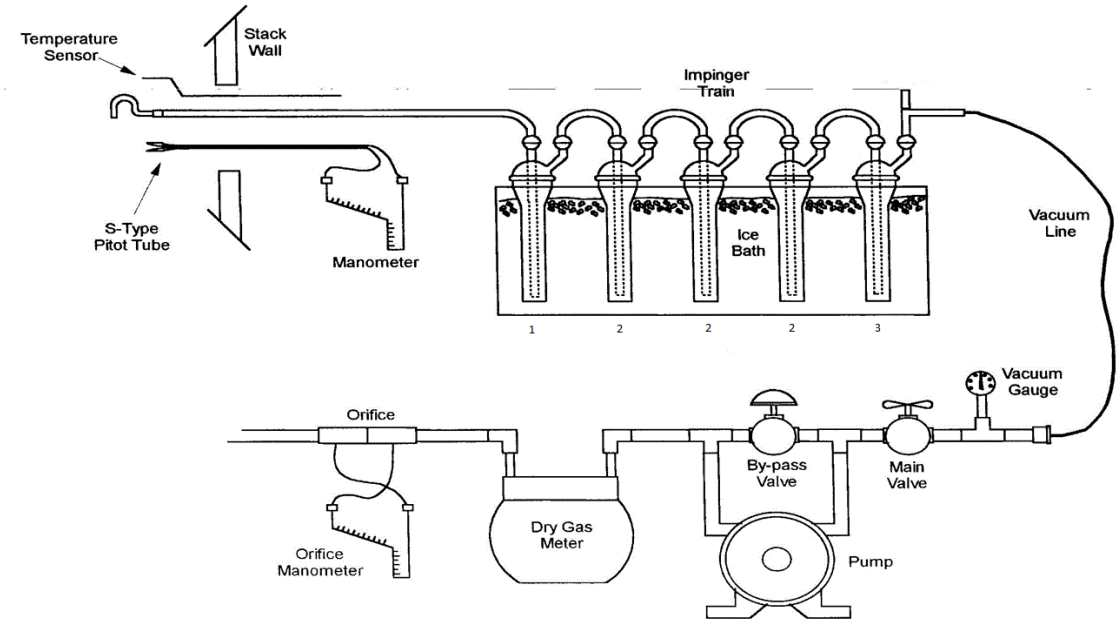


Figure 1. Principle of sampling arrangement, 1. condenser; 2. Absorbers; 3 silica gel

5.3.1 Probe

Unheated probe and entry nozzle without filter shall fulfil the requirements of EN 13284-1 excluding nozzle internal diameter which may be less than 6 mm. Nozzle i.d.'s less than 3.5 mm should be avoided. Area of nozzle entry should be specified in accuracy better than ±10 %.

Table 2 Evaluation of needed nozzle diameter at different flow gas velocities.

Nozzle size (diameter, mm)											
	sampling rate (l/min)										
Flow rate (m/s)	**0,2**	**0,5**	**1**	**2**	**4**	**6**	**8**	**10**	**12**	**16**	**20**
2	1,5	2,3	3,3	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	1,0	1,6	2,3	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	0,8	1,3	1,9	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	0,7	1,2	1,6	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	0,7	1,0	1,5	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	0,6	0,9	1,3	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	0,6	0,9	1,2	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	0,5	0,8	1,2	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	0,5	0,8	1,1	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	0,5	0,7	1,0	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

The probe should be about 0.5-1 meter longer than the diameter of duct. If two opposed sampling ports are available half of the duct diameter + 0.5- 1 m is adequate for the sampling probe

Accepted material of probe and nozzle is stainless steel (316 SS and 316l SS) or boron or quartz glass. Some minor parts as fitting and seals may be PTFE, otherwise it should be avoided. However, on very large ducts PTFE lines use may be necessary for the practical reasons, e.g. when moving the probe inside the duct. On that case internal volume of PTFE tube should be minimized and number of blanks and washing practises evaluated. Internal diameter and length of probe should be minimized.

The probe may be marked before sampling in order to reach more easily the representative measurement point(s) in the measurement plane. It is important to specify the direction of nozzle entry.

If sampling is performed from the highly negative pressure duct, back flush from the absorbers into the duct is possible before and after the sampling sequence when pump is stopped. To avoid this, the connection between the probe and absorbers should be easily detached or suitable inert valve is recommended.

5.3.2 Condenser and absorber

To achieve an efficient absorption at least condenser and three absorbers shall be placed in series. Temperature of condensate flask and absorbers shall be cooled less that 5°C during the sampling.

On condenser and absorbers the inner tube should reach the bottom of the impinger and end to bubble breaker or sintered frit to fine the bubbles.

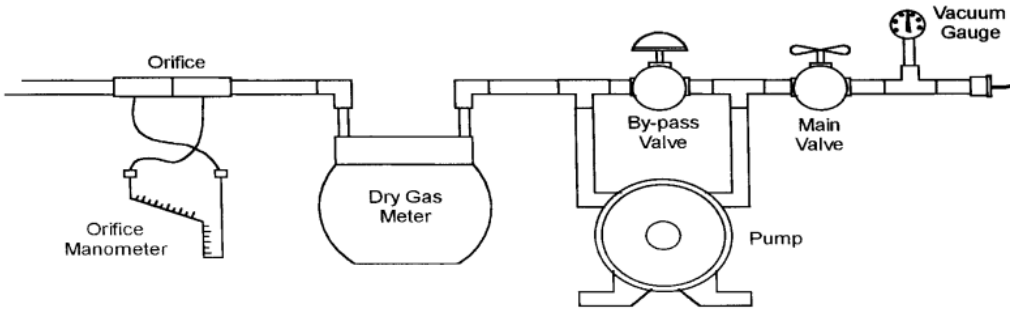
Recommended size of impingers should be capable of sampling on isokinetic flow rates without significant overflow of absorbent liquids. Recommended size of impingers is about 500 ml/impinger and absorber liquid volume of 300 ml. Condensate flasks may be bigger especially in high humidity and a long sampling periods. Extra protection bottle is recommended before silica gel.

When sampling hot gas or at warm conditions, extra cooler may be added before the condensate flask to avoid excessive break though of moisture from condensate flask into absorbers.

Absorption efficiency and carry out may be tested by analysing the last absorber separately. This may be hard to obtain for all analytes due to low concentration of analytes. In that case the analyte of highest concentration may be used for the evaluation, e.g. the main solvent amine. Breakthrough in the last bottle should not exceed 5 % from total amount.

5.3.3 Sampling pump

Leak-free pump capable of sampling gas at a set flow rate.
NOTE. A rotameter (optional) facilitates the adjustment of the nominal sampling flow rate.



5.3.4 Gas volume meter

Dry or wet gas volume meter may be used providing the volume is measured with a relative uncertainty of calibration not exceeding 2 % at actual conditions. The gas volume-meter shall be equipped with a temperature measuring device (uncertainty of calibration less than 2.5 K). The absolute pressure at the gas volume meter (uncertainty of calibration less than 1.0 %) can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10.5 °C or a volume content $\chi(H_2O)$ = 1.25 %).

For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at 110 °C for at least 2 h.
When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

The relative pressure can be neglected if the gas volume meter is the last equipment of the sampling chain.

5.3.5 Absorption reagents

Absorbent is 0.1 M sulfamic acid. Acidic conditions hinder the evaporation of analytes.

Solid sulfamic acid shall be added into condensate flask before sampling. The amount of sulfamic acid into condenser is 1000 mg/100 ml of expected amount of condensate. Small amount of UHQ water may be added into condensate flask before the sampling to dissolve sulfamic acid.

5.4 Sampling procedure

5.4.1 Preparation and installation of equipment

5.4.1.1 Sampling location and sampling points

The sampling location is chosen according to EN 15259. A grid measurement is performed if homogeneity of sample gas is not validated.

5.4.2 Sampling procedure

5.4.2.1 Preparation

Homogeneity in the sampling plane should be evaluated before sampling as well as development of flow (direction, turbulence). Size and the arrangement of the duct shall be measured and recorded.

Humidity of the flue gas should be estimated or measured. Based on the sampling time and humidity, expected amount of condensate during the sampling should be calculated. Solid sulfamic acid is added into the condensate bottle focusing the target concentration of 0.1 M. In practice this means 0.1 g sulfamic acid must be added to every 10 ml condensate.

*Example. Calculated total condensate amount in sampling is 120 ml. Amount of sulfamic acid added into the condenser is 120ml/10ml * 0.1 g = 1.2 g.*

Required space is reserved before the sampling. Ice bath shall be cooled before the sampling.

Fill the absorbers at the clean area. Proposed amount of absorbent in the impinger is 60 % of the total volume, e.g. at 500 ml impinger recommended absorbent volume is 300 ml.

5.4.2.2 Checks

Check the velocities of flow at the sampling points, and calculate the sampling parameters to be achieved at each point (volume flow rate, sampling time), if required.

Ensure that the sampling train has been correctly assembled, and is leak tight, performing leak tests before each sample. Leak test shall be performed as below:

a) Assemble the complete sampling system, including absorbers
b) Seal the nozzle, or if not practicable, a connection between the condensate flask and probe air tightly.
c) Switch on the pump
d) Observe the rotameter / gas meter. Leak shall not exceed 2 % of the expected gas flow rate.
e) Release the seal SLOWLY and let under pressure disappear from the sampling system BEFORE turning pump off to avoid back flush of absorbers. Fast release of under pressure may break the bottom of flat glass absorbers.
f) Turn off the pump

5.4.2.3 Field blank

This procedure is used to ensure that no significant contamination has occurred during all the steps of the measurement.

A field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this report. This includes the sampling procedure without the suction step.

If sampling system in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken before each measurement series. The blank taken after a measurement series may be used as the blank taken before the following measurement series.

The average sampling volume shall be used for calculation of the blank value expressed in $\mu g/m^3n$.

If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank.

Also sample from wash water, absorbent liquids and sulfamic acid used on measurement should be stored as blank samples. These will be analysed if field blank shows unexpected positive concentrations.

5.4.2.4 Sampling

Taking into account the expected concentration related to analytical detection limit and flue gas flow, calculate the required sample volume and time. Suggested sampling rate depends on the design of the absorption flasks. In practice sampling rate of 5-7 l/min and sampling time of 1-2 hours are applicable. Longer sampling times up to 6-8 hours may be required if lower concentrations at the level less than 5 $\mu g/m^3n$ are expected.

Sampling procedure is as follows:

a) Record the gas meter values, temperature, pressure, startup time
b) Insert the probe in the duct. If sampling will not start immediately turn the nozzle pointing to the downstream of the flow before the sampling
c) Turn on the sampling pump
d) On the conditions of strong negative pressure, connect the absorbers and the probe or open the valve between
e) Adjust the sample flow to required value
f) On grid measurement move the probe and adjust the flow rate accordingly without stopping the pumps
g) Maintain the temperature of ice-bath at required level
h) At the end of sampling, turn off the pump. On ducts of strong negative pressure disconnect the probe and absorbents before stopping the pump. At the end of sampling record the final gas meter readings
i) Wash the probe by following procedure, if possible,:
    a. Take the probe out from the duct
    b. Turn on the sampling pump
    c. Add portion of absorption liquid into the nozzle (about 10 ml) using washing bottle or suchlike
    d. Let the washing liquid run to the condenser and stop the pump. Pump values on washing are not included the total sample amount!
    e. If the probes are impractical to take out of the duct between the sampling periods, and in the case of negative pressure in the duct, add clean UHQ water from the absorber end of the probe to wash the probe.
j) Pour the condensate into the storage vessel. Plastic air tight vessels may be used.
k) Pour the absorbent liquids excluding the last absorbent into the storage vessel. NOTE! The condensate and absorption liquids are not combined. Last absorption vessel shall be stored at separate vessel.
l) Wash the condensate bottle by UHQ water and pour the washing into the storage vessel of condensate. Wash the absorbers respectively by absorbent solution.

5.4.2.5 Storage of samples

Samples should be stored in cold. Frozen is recommended. Analysis should be performed as soon as possible.

6. SAMPLE PREPARATION

6.1 Principle

The samples will consist of water based condensate and absorbent which both are treated separately and spiked with deuterated internal standards. Analysis is done with direct injection to UPLC-MS/MS.

The deuterated internal standards are added into the sample vial before analysis. For the samples containing solids filtering may be applied.

Note: High concentration (over 0.5 %) of solvent amines may interfere with the analysis.

6.2 Reagents and materials

6.2.1 Laboratory equipment

- Standard laboratory glassware such as Erlenmeyer flasks and beakers
- Balances with appropriate range and precision
- Pipettes
- Millipore MilliQ water cleaning system or other UHQ water source

6.2.2 Reagents

Solvents and reagents of sufficient purity shall be used, for example

- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- Acetonitrile (BDH Prolabo (LC-MS grade) or equivalent)
- UHQ water (Millipore or equivalent)
- Sulfamic acid

6.2.3 Standards

High purity standards shall be used, for example

- Diethylamine (DEN), (Chem Service Inc.) O-2046, Purity 99,5 %
- Dimethylamine (DMA), (Acros Organics), 2M in methanol
- Ethylamine (EA), (Acros Organics), 2M in THF
- Methylamine (MMA), (AccuStandard Inc.) M-1666A-DI-R-ADD1, 2510 µg/mL (in water)
- Triethylamine (TEA), (Chem Service Inc.) O-297, Purity 99,5 %
- Trimethylamine (TMA), (Alfa Aesar GmbH & Co KG) H27324 33 % in ethanol

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

6.2.4 Internal standards (ISTD)

High purity standards shall be used, for example

- Diethylamine D10, (C/D/N Isotopes Inc.), D-2137, purity 98 %
- Triethylamine D15, (C/D/N Isotopes Inc.), D-1221, purity 98 %
- Methyl-d3-amine HCl (C/D/N Isotopes Inc.), D-279, purity >99 %
- Dimethyl-d6-amine HCl (C/D/N Isotopes Inc.), D-5090, purity 99%
- Trimethyl-d9-amine HCl (C/D/N Isotopes Inc.), D764, purity >99%

Mixture containing 10 mg/l of each component in methanol can be stored in freezer.

6.3 Procedure, aqueous samples and flue gas samples

An aliquot of aqueous sample (e.g. absorbent and condensate from flue gas sampling) is injected to analysis vial and diluted with methanol to final consistency of 10 % methanol and analysed by UPLC-MS/MS. Internal standard is added into analysis vial before analysis.

6.3.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.3.2 Quality control

Standard addition to the sample matrix will be done with each sample set. Recoveries will be monitored.

6.3.3 Pretreatment and cleaning

The total sample volume shall be measured with a suitable analytical balance. An aliquot of 900 µL is injected to vial, internal standards (in methanol) are added e.g. 50 µL of 1 mg/L solution and methanol is added to final volume of 1000 µL. If precipitation is observed the sample is filtered thru a disposable syringe filter (0.2 µm).

A spiked (standard addition at desired level) sample is done to the sample matrix.

For wash water and solvent amine samples procedures are as above except samples may require dilution due to expected high concentration (over 0.2 %) of solvent amines in the sample.

7. INSTRUMENTAL ANALYSIS

7.1 Instruments and chemicals

UPLC-MS/MS apparatus is used in all analyses and a minimum of two transitions per analyte is monitored (when possible). Chromatographically complete separation of analytes is challenging and it is likely that some overlapping will occur. The UPLC conditions used are as followed:

- Column: Supelco Discovery® HS F5 (150 x 2.1 mm, 3 µm)
- Column temperature: 40 ºC
- Eluents: 0.02 % HCOOH in UHQ (A) and 0.02 % HCOOH in acetonitrile (B)
- Injection volume: 5 µL
- Flow rate: 0.4 mL/min
- Gradient 95/5 (A%/B%) for 5 min, 75/25 at 6 min, 30/70 at 12 min, 10/90 at 13 min and 95/5 at 14 min. Total run time 15 min

Applicable start point for the settings in ion source are (Waters Xevo):

Ionisation	Electro spray ionisation (ESI)	
Source temp	150	ºC
Desolvation temp	600	ºC
Capillary voltage	0,5	kV
Desolvation flow	1000	L/h
Cone flow	50	L/h

7.2 Calibration

7.2.1 Calibration references

Standard solutions will be done at 10 mg/l concentration in methanol.
External standards are diluted to the range of 10-500 µg/L. Calibration should be carried out with at least four calibration solutions. These solutions contain all native and all but one deuterated alkylamine standards in precisely defined amounts.

Applicable concentration of labeled internal standard solution is 1 mg/l when 50 µl is injected into analysis vials.

7.3 Procedure

Analysis of samples is done with UPLC-MS/MS system and minimum of two transitions is monitored (excluding methylamine and methylamine D3):

- Diethylamine (DEN): 74,16 → 45,92 and 74,16 → 28,88
- Dimethylamine (DMA): 46,16 → 45,92 and 46,16 → 29,933
- Ethylamine (EA): 46,16 → 28,89 and 46,16 → 26,84
- Methylamine (MMA): 32,03 → 31,90
- Triethylamine (TEA): 102,22 → 73,95 and 102,22 → 57,91
- Diethylamine D10: 84,20 → 51,94 and 84,20 → 33,92
- Methylamine D3: 34,97 → 34,86
- Triethylamine D15: 117,30 → 64,89 and 117,30 → 85,03
- Trimethylamine D9: 69,03 → 49,00 and 69,03 → 51,03

7.4 Quality assurance

Recoveries of internal standards and the recoveries of standard additions and blank values are monitored.

8. RESULTS

8.1 Calculations

Results are calculated with internal standard correction with TargetLynx software or corresponding by using quantification method for alkylamines. Final results will be given in units corresponding to concentration of sample.

8.2 Limit of quantification

Limit of quantification is dependent of the sample matrix and is generally between 5 and 10 µg/L given as concentration of the LC vial.

8.2.1 Sample amount

$$Q_{analyte} = C \times V_s$$

$Q_{analyte}$	quantity of amine collected, in micrograms;
C	is the concentration of the solution in micrograms per millilitre;
V_s	is the volume of absorption solution in millilitres

8.2.2 Sample gas volume

For dry gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_{res}}{101{,}3}$$

For wet gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_s(H_2O)}{101{,}3}$$

Where

V_{std}	the volume under standard conditions and dry basis, in cubic metres (m^3)
V_{Tp}	the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m^3);
T	Actual temperature in Kelvins
p	Total pressure in kPa at the gas meter
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);
P_{res}	is the residual vapour pressure, in kilopascals (kPa).

8.2.3 Final concentration

Final concentration in the flue gas is expressed as:

$$C_{analyte}\ [\mu g/m^3 n] = \frac{Q_{analyte}}{V_{std}}$$

8.3 Overall method uncertainty

Tested accuracy was ±25 % without labelled internal standards. The use of labelled standards improved the accuracy significantly, but only few datasets has been analysed using all internal standards and exact value cannot be presented.

Estimation of overall uncertainty including sampling is ±30 - 50 %.

APPENDIX 4
SAMPLING AND ANALYSIS OF ALDEHYDES

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1. INTRODUCTION

This report presents the current sampling and analysis methods developed by Ramboll Analytics for formaldehyde and acetaldehyde emitting from the ducts and stacks. Methods may also be applied for the analysis of wash water and solvent in amine based post combustion capture processes (PCC).

2. SCOPE

The proposed method specifies the sampling, extraction and analysis procedures of formaldehyde and acetaldehyde in monoethanolamine (MEA) based CCS-plant flue gas.

The method has been designed to measure aldehyde concentrations of 50 ng/m^{3}n in stationary source emissions.

Two different analysis methods are proposed. The method according to EPA 0011/8315A on which the sampling is done into an acidic dinitrophenylhydrazine (DNPH) solution and extracted with dichloromethane. The other method being the sampling into commercial solid absorbent coated with DNPH. The analysis of samples can be done with HPLC-UV or UPLC-MS/MS.
The analytical methods proposed are applicable for analysis of amine based CCS-plant flue gas.

Table 1. Scope of analytes

Compound	**CAS-number**	**Max. MEA concentration the liquid sample**	**Detection limit µg/m^{3}n, sample volume 0,5 m^{3}n**
Formaldehyde	50-00-0	10 %	0.050
Acetaldehyde	75-07-0	10 %	0.050

3. NORMATIVE REFERENCES

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13284-1:2001, Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report

EN ISO 3696:1995, Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)

EPA Method 0011, "Sampling for selected aldehyde and ketone emissions from stationary sources"

4. TERMS AND DEFINITIONS

4.1 Abbreviations

AMP	2-Amino-2-methyl-1-propanol
DCM	Dichloromethane
DEA	Diethanolamine
DEN	Diethylamine
DL	Detection Limit
DMA	Dimethylamine
DNPIPA	N,N´-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
IDL	Instrument Detection Limit
LMW	Low Molecular Weight
MDEA	N-Methyldiethanolamine
MDL	Method Detection Limit
MEA	Monoethanolamine
MeOH	Methanol, methyl alcohol
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
PCC	Post combustion CO_2-capture
RI	Refractive Index
SIM	Single-ion monitoring
SPE	Solid-Phase Extraction
T_b	Boiling point
TMA	Trimethylamine
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
vis	Visible

4.2 Terms and definitions

4.2.1 Solvent amine(s)

Common name used in this study for alkanolamines.

4.2.2 Isokinetic sampling

Sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as the velocity and direction of the gas in the duct at the sampling point.

4.2.3 Analytical blank value

Value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all relevant reagents and materials.

4.2.4 Limit of detection (LOD)

Minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability.

The measurement value can be distinguished from the analytical blank value with a confidence of 99%, when the limit of detection is expressed as the mean analytical blank value plus three times the standard deviation of the analytical blank.
The limit of detection should preferably be calculated from the analytical blank. If this is not possible, the limit of detection can be calculated from the signal to noise ratio.

4.2.5 Limit of quantification (LOQ)
Limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus five to ten times the standard deviation of the analytical blank. The limit of quantification should preferably be calculated from the analytical blank. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio.

5. SAMPLING

5.1 Principle and minimum requirements

The test programme shall be established following the advice and requirements described in EN 15259:2007 (5.4, Clauses 6, 7 and 8).

Sampling should be carried out at one or several points in the sampling section, in accordance of the test of homogeneity carried out according the EN 15259.

Sampling is performed by using ambient temperature probe with a nozzle of know internal diameter, chilled condensate and absorption section, gas drying and sample gas volume measurements. A solid preservation chemical is added into condensate flask before sampling.

If sample gas will certainly not include drops, droplets or solid matter sampling may be performed as non-isokinetic sampling.

5.2 Side reactions during sampling

According to EPA method 0011:

A decomposition product of 2,4-dinitrophenylhydrazine, 2,4-dinitroaniline, can interfere if concentrations are high. The 2,4-dinitroaniline can co-elute with the 2,4-dinitrophenylhydrazone of formaldehyde under the high performance liquid chromatography
conditions used for the analysis. High concentrations of highly oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde, and that also absorb at 360 nm, will interfere with the analysis.

Formaldehyde, acetone, and 2,4-dinitroaniline contamination of the aqueous acidic 2,4-dinitrophenylhydrazine (DNPH) reagent is frequently encountered. The reagent must be prepared within five days of use in the field and must be stored in an uncontaminated environment both before and after sampling, in order to minimize blank problems. Some concentration of acetone contamination is unavoidable, because acetone is ubiquitous in laboratory and field operations. However, the acetone contamination must be minimized.

Dimethylolurea creates a slight positive interference; and hexamethylenetetramine and paraformaldehyde significantly interfere with the determination of formaldehyde. These compounds can decompose in the acidic reagent used to collect the sample to form formaldehyde;

Tolualdehyde interferes with the determination of acetophenone because they coelute chromatographically;

High levels of nitrogen dioxide can interfere by consuming all reagents.

5.3 Sampling train and its operations

Principle of the sampling train is presented at the Figure 1.

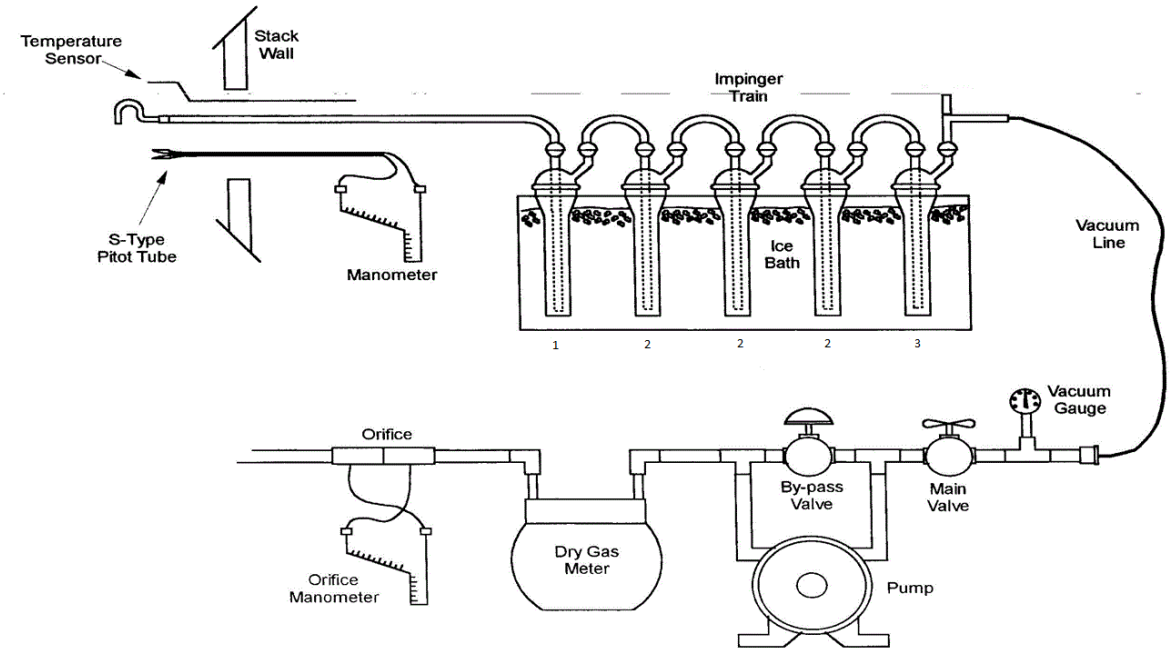


Figure 1. Principle of sampling arrangement, 1. condenser; 2. Absorbers; 3 silica gel

5.3.1 Probe

Unheated probe and entry nozzle shall fulfil the requirements of EN 13284-1 excluding nozzle internal diameter which may be less than 6 mm. Nozzle i.d.'s less than 3.5 mm should be avoided. Area of nozzle entry should be specified in accuracy better than ±10 %.

Table 2 Evaluation of needed nozzle diameter at different flow gas velocities.

	Nozzle size (diameter, mm)										
	sampling rate (l/min)										
Flow rate (m/s)	**0,2**	**0,5**	**1**	**2**	**4**	**6**	**8**	**10**	**12**	**16**	**20**
2	1,5	2,3	3,3	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	1,0	1,6	2,3	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	0,8	1,3	1,9	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	0,7	1,2	1,6	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	0,7	1,0	1,5	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	0,6	0,9	1,3	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	0,6	0,9	1,2	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	0,5	0,8	1,2	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	0,5	0,8	1,1	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	0,5	0,7	1,0	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

The probe should be about 0.5-1 meter longer than the diameter of duct. If two opposed sampling ports are available half of the duct diameter + 0.5 - 1 m is adequate for the sampling probe

Accepted material of probe and nozzle is stainless steel (316 SS and 316l SS) or boron or quartz glass. Some minor parts as fitting and seals may be PTFE, otherwise it should be avoided because possible corrosion by solvent amines. However, on very large ducts PTFE lines use may be necessary for the practical reasons, e.g. when moving the probe inside the duct. On that case internal volume of PTFE tube should be minimized and number of blanks and washing practises evaluated. Internal diameter and length of probe should be minimized.

The probe may be marked before sampling in order to reach more easily the representative measurement point(s) in the measurement plane. It is important to specify the direction of nozzle entry.

If sampling is performed from the highly negative pressure duct, back flush from the absorbers into the duct is possible before and after the sampling sequence when pump is stopped. To avoid this, the connection between the probe and absorbers should be easily detached or suitable inert valve is recommended.

5.3.2 Condenser and absorber

To achieve an efficient absorption at least condenser and three absorbers shall be placed in series. Temperature of condensate flask and absorbers shall be cooled less that 5°C during the sampling.

On condenser and absorbers the inner tube should reach the bottom of the impinger and end to bubble breaker or sintered frit to fine the bubbles.

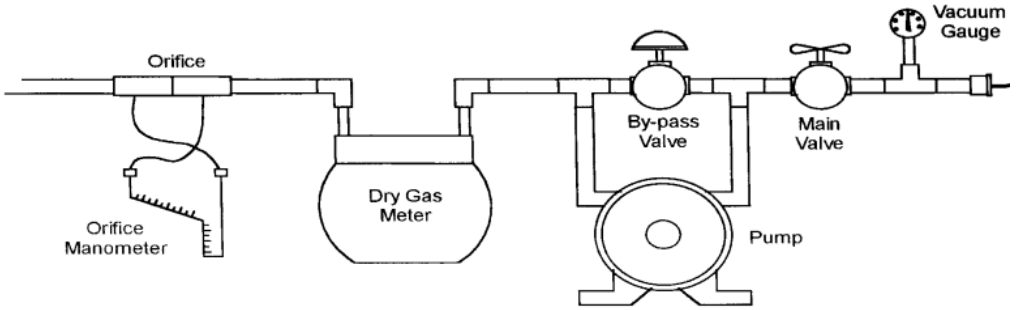
Recommended size of impingers should be capable of sampling on isokinetic flow rates without significant overflow of absorbent liquids. Recommended size of impingers is about 500 ml/impinger and absorber liquid volume of 200 ml for the first impinger and 100 ml for the second and the third. Condensate flasks may be bigger especially in high humidity and a long sampling periods. Extra protection bottle is recommended before silica gel.

When sampling hot gas or at warm conditions, extra cooler may be added before the condensate flask to avoid excessive break though of moisture from condensate flask into absorbers.

Absorption efficiency and carry out may be tested by analysing the last absorber separately. This may be hard to obtain for all analytes due to low concentration of analytes. In that case the analyte of highest concentration may be used for the evaluation, e.g. the main solvent amine. Breakthrough in the last bottle should not exceed 5 % from total amount.

5.3.3 Sampling pump

Leak-free pump capable of sampling gas at a set flow rate.
NOTE. A rotameter (optional) facilitates the adjustment of the nominal sampling flow rate.



5.3.4 Gas volume meter

Dry or wet gas volume meter may be used providing the volume is measured with a relative uncertainty of calibration not exceeding 2 % at actual conditions. The gas volume-meter shall be equipped with a temperature measuring device (uncertainty of calibration less than 2.5 K). The absolute pressure at the gas volume meter (uncertainty of calibration less than 1.0 %) can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10.5 °C or a volume content X(H_2O) = 1.25 %).

For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at 110 °C for at least 2 h.
When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

The relative pressure can be neglected if the gas volume meter is the last equipment of the sampling chain.

5.3.5 Absorption reagents

For formaldehyde and acetaldehyde 1 L of aqueous acidic DNPH absorbent is made according to guidelines presented in EPA method 0011. Note: All glassware must be rinsed with acetonitrile and e.g. acetone must not be used in any preparation step. As DNPH reacts also with ketones and other compounds containing the carbonyl group.

The absorbent is prepared by adding 500 mL of UHQ-water into a suitable glass container previously washed with acetonitrile. The container is kept under constant agitation with high stirring rate on a magnetic stirrer. 175 mL of concentrated hydrochloric acid is mixed slowly with water and approximated amount of 1,4-dinitrophenylhydrazine (DNPH), enough to make a saturated solution, is weighed to the acidic water. UHQ –water is added to the 1 L mark and the solution is stirred overnight. If all crystals are dissolved, additional amount of DNPH must be added and stirring continued until solution is saturated. Solution is filtrated with the aid of vacuum. Before use possible aldehyde contaminations are removed by washing the solution twice with dichloromethane and once with cyclohexane. An aliquot of the absorbent is analysed with the actual samples as a blank sample.

NOTE! DNPH crystals and DNPH solution are potential carcinogens and should be handled with plastic gloves at all times, with prompt and extensive use of running water in case of skin exposure.

5.4 Sampling procedure

5.4.1 Preparation and installation of equipment

5.4.1.1 Sampling location and sampling points

The sampling location is chosen according to EN 15259. A grid measurement is performed if homogeneity of sample gas is not validated.

5.4.2 Sampling procedure

5.4.2.1 Preparation

Homogeneity in the sampling plane should be evaluated before sampling as well as development of flow (direction, turbulence). Size and the arrangement of the duct shall be measured and recorded.

Required space is reserved before the sampling. Ice bath shall be cooled before the sampling.

Fill the absorbers at the clean area. Proposed amount of absorbent in the impinger is 60 % of the total volume, e.g. at 500 ml impinger recommended absorbent volume is 300 ml.

5.4.2.2 Checks

Check the velocities of flow at the sampling points, and calculate the sampling parameters to be achieved at each point (volume flow rate, sampling time), if required.

Ensure that the sampling train has been correctly assembled, and is leak tight, performing leak tests before each sample. Leak test shall be performed as below:

a) Assemble the complete sampling system, including absorbers
b) Seal the nozzle, or if not practicable, a connection between the condensate flask and probe air tightly.
c) Switch on the pump
d) Observe the rotameter / gas meter. Leak shall not exceed 4 % of the expected gas flow rate.
e) Release the seal SLOWLY and let under pressure disappear from the sampling system BEFORE turning pump off to avoid back flush of absorbers. Fast release of under pressure may break the bottom of flat glass absorbers.
f) Turn off the pump

5.4.2.3 Field blank

This procedure is used to ensure that no significant contamination has occurred during all the steps of the measurement.

A field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this report. This includes the sampling procedure without the suction step.

If sampling system in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken before each measurement series. The blank taken after a measurement series may be used as the blank taken before the following measurement series.

The average sampling volume shall be used for calculation of the blank value expressed in $\mu g/m^3n$.

If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank.

Also sample from wash water, absorbent liquids and sulfamic acid used on measurement should be stored as blank samples. These will be analysed if field blank shows unexpected positive concentrations.

5.4.2.4 Sampling

Taking into account the expected concentration related to analytical detection limit and flue gas flow, calculate the required sample volume and time. Suggested sampling rate depends on the design of the absorption flasks. In practice sampling rate of 5-7 l/min (max 28 l/min) and sampling time of 0,5-2 hours are applicable.

If unsure, calculate the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement.

Sampling procedure is as follows:

a) Record the gas meter values, temperature, pressure, startup time
b) Insert the probe in the duct. If sampling will not start immediately turn the nozzle pointing to the downstream of the flow before the sampling
c) Turn on the sampling pump
d) On the conditions of strong negative pressure, connect the absorbers and the probe open the valve between
e) Adjust the sample flow to required value
f) On grid measurement move the probe and adjust the flow rate accordingly without stopping the pumps
g) Maintain the temperature of ice-bath at required level
h) At the end of sampling, turn off the pump. On ducts of strong negative pressure disconnect the probe and absorbents before stopping the pump. At the end of sampling record the final gas meter readings
i) Wash the probe by following procedure, if possible,:
    a. Take the probe out from the duct
    b. Turn on the sampling pump
    c. Add portion of absorption liquid into the nozzle (about 10 ml) using washing bottle or suchlike
    d. Let the washing liquid run to the condenser and stop the pump. Pump values on washing are not included the total sample amount!
    e. If the probes are impractical to take out of the duct between the sampling periods, in the case of negative pressure in the duct, add clean UHQ water from the absorber end of the probe to wash the probe.
j) Pour the condensate into the storage vessel. Plastic or glass (for the absorption solution) vessels may be used if sample is immediately frozen. Other cases glass vials with inert and air tight cap shall be used.
k) Pour the absorbent solvents excluding the last absorbent into the storage vessel. NOTE! The condensate and absorption liquids are not combined. Last absorption vessel shall be stored at separate vessel.
l) Wash the condensate flask by UHQ water and pour the washing into the storage vessel of condensate. Wash the absorbers respectively with methanol or absorbent solution.

5.4.2.5 Storage of samples

Samples should be stored in cold. Frozen is recommended. Analysis should be performed as soon as possible.

6. SAMPLE PREPARATION

6.1 Principle

The determination of the aldehydes is based on quantification of derivatized analytes with external standards using UPLC-MS/MS (or HPLC-UV).

6.2 Reagents and materials

6.2.1 Laboratory equipment

- Standard laboratory glassware such as Erlenmeyer flasks and beakers
- Balances with appropriate range and precision
- Pipettes
- Vials for sample extracts
- Millipore MilliQ water cleaning system
- TurboVap -automated solvent evaporation system
- LiChrolut EN 500 mg/6ml (Merck)
- Sep-Pak DNPH-Silica cartridges Plus 360 mg (Waters)

6.2.2 Reagents

Solvents and reagents of sufficient purity shall be used, for example

- Acetonitrile (J.T. Baker or equivalent)
- 2,4-dinitrophenylhydrazine ≥ 99% (Sigma-Aldrich No. 42210-100G-F)
- Dichloromethane (J.T. Baker (high purity) or equivalent)
- Hydrochloric acid (J.T. Baker (high purity) or equivalent)

6.2.3 Standards

High purity standards shall be used, for example

- 2,4-DNPH-formaldehyde, 100 µg/ml, solvent acetonitrile, purity 99,9 % (Supelco No. 47177)
- 2,4-DNPH-acetaldehyde, 1 000 µg/ml, solvent acetonitrile, purity 99,9 % (Supelco No. 47340-U)

6.2.4 Internal standards (ISTD)

Isotope labeled internal standards may be, however not obligatory.

6.3 Procedure, EPA method

According to EPA 8315A: An aliquot of acidic DNPH sample is measured into a separating funnel and extracted with dichloromethane, washed, evaporated and analysed.

6.3.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.3.2 Quality control

Standard addition to synthetic sample matrix will be done with each sample set. Recoveries will be monitored.

6.3.3 Pretreatment and cleaning

An aliquot of sample is weighed to a separate container and extracted three times with dichloromethane. Depending on the concentration of the analytes either an aliquot of the dichloromethane phase is diluted into mobile phase or the dichloromethane is concentrated by evaporation and solvent exchanged into acetonitrile. During evaporation step precipitation can occur and therefore dichloromethane can be pre-washed with 1 M hydrochloric acid (not mentioned in EPA method).

6.4 Procedure, solid DNPH sorbent and condensate

The commercial solid sorbent is extracted with acetonitrile, evaporated and analysed. The condensate sample is extracted with DNPH coated SPE cartridges, eluted, evaporated and analysed.

6.4.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.4.2 Quality control

Standard addition to synthetic sample matrix and to DNPH cartridge will be done with each sample set. Recoveries will be monitored.

6.4.3 Pretreatment and cleaning

Solid sorbent

The cartridge is eluted with acetonitrile which is evaporated to the volume of 500 µL with TurboVap concentration workstation. Sample is diluted with UHQ-water to final volume of 1000 µL, placed into LC vial and analysed.

Condensate

The whole condensate sample will be analysed and therefore the sample container is weighed when full and when empty.
A stock DNPH-solution is prepared by dissolving approximately 0,6 g of DNPH into 50 mL of hydrochloric acid:UHQ-water:ACN mixture (2:5:1) and a working solution (0,05 g/L) is prepared by appropriate dilution of the stock solution with UHQ-water.
Lichrolut EN cartridges are conditioned with 5 mL of ACN and with 10 mL of UHQ-water followed by 20 mL of the DNPH working solution. Before the sample is loaded into the cartridge the pH of the sample is adjusted to 1,5 with 1 M hydrochloric acid. The sample is loaded into the cartridge slowly and the cartridge is dried with gentle flow of high purity nitrogen. The aldehyde derivatives are extracted with 7 mL of acetonitrile. Diluted to known amount of 50/50 ACN/UHQ and analysed.
Note: For unknown samples two DNPH derivatized LiChrolut EN cartridges can be connected in series to verify possible breakthrough

7. INSTRUMENTAL ANALYSIS

7.1 Instruments and chemicals

If the UPLC-MS/MS apparatus is used in analyses a minimum of two transitions per analyte is monitored.

The UPLC conditions used are as followed:

- Column: Waters Acquity UPLC BEH C18 1,7 µm (2,1 x 100 mm)
- Column temperature: 40 ºC
- Eluents: 0,02 % HCOOH in UHQ (A) and 0,02 % HCOOH in acetonitrile (B)
- Injection volume: 5 µL
- Gradient: 70/30 (A%/B%) for 1,5 min, 50/50 at 6 min, 0/100 at 10 min, 70/30 at 12 min. Total run time 14 min
- Applicable start point for the settings in ion source are (Waters Xevo):

Ionisation	Electro spray ionisation (ESI)	
Source temp	150	ºC
Desolvation temp	600	ºC
Capillary voltage	3,6	kV
Desolvation flow	1000	L/h
Cone flow	50	L/h

Also HPLC-UV can be utilized with the following parameters:
- Column: Waters Ltd. µBONDAPAK C18 10µm 125Å 3,9×300mm
- Column temperature: 40 ºC
- Eluents: UHQ Water (A) and 100 % acetonitrile (B)
- Injection volume: 10 µL
- Flow: 1.2 ml/min
- Gradient: 100/0 (A%/B%) for 1 min, change during 13 min to final concentration of 80/20. Total run time 14 min
- Ambient temperature

7.2 Calibration

Calibration references
Standard solutions will be done at 10 mg/l concentration in acetonitrile.
External standards are diluted to the range of 10-1000 µg/L. Calibration should be carried out with at least four calibration solutions.

7.3 Procedure

Analysis of samples is done with UPLC-MS/MS system and minimum of two transitions is monitored:
- DNPH-Formaldehyde: 209.16 → 151.04 and 209.16 → 163.03
- DNPH-Acetaldehyde: 223.16 → 151.14 and 223.16 → 163.01

7.4 Quality assurance

Recoveries of standard additions and blank values are monitored.

8. RESULTS

8.1 Calculations

Results are calculated with TargetLynx software or corresponding by using quantification method for aldehydes. Final results will be given in units corresponding to concentration of sample.

8.1.1 Sample amount

$$Q_{analyte} = C \times V_s$$

$Q_{analyte}$	quantity of aldehyde collected, in micrograms;
C	is the concentration of the solution in micrograms per millilitre;
V_s	is the volume of absorption solution in millilitres

8.1.2 Sample gas volume

For dry gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_{res}}{101{,}3}$$

For wet gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_s(H_2O)}{101{,}3}$$

Where

V_{std}	the volume under standard conditions and dry basis, in cubic metres (m³)
V_{Tp}	the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m³);
T	Actual temperature in Kelvins
p	Total pressure in kPa at the gas meter
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);
P_{res}	is the residual vapour pressure, in kilopascals (kPa).

8.1.3 Final concentration

Final concentration in the flue gas is expressed as:

$$C_{analyte}\ [\mu g/m^3n] = \frac{Q_{analyte}}{V_{std}}$$

8.2 Limit of quantification

If care has been taken in cleaning of equipment the LOQ-value between 5-10 µg/L can be reached corresponding to the concentration of the extract in LC vial. But especially formaldehyde can be seen in blanks typically originating form glassware, contaminated solvents, etc. This will naturally raise the LOQ.

8.3 Overall method uncertainty

Expected method performance based on dual trains (EPA 0011)

Compound	Precision (%RPD)[1]	Accuracy (%)[2]	Detection Limit (ppbv)[3]
Formaldehyde	±21	±10	±90
Acetaldehyde	±17	±21	±40

1) *Relative per cent difference limit for dual trains*
2) *Limit for field spike recoveries.*
3) *The lower reporting limit having less than 1% probability of false positive detection.*

9. BIBLIOGRAPHY

- EPA Method 0011, "Sampling for selected aldehyde and ketone emissions from stationary sources"
- Banos, C.E., Silva, M., J. Chromatogr. A 1216 (2009) pp. 6554-6559
- EPA Method 0011, "Sampling for selected aldehyde and ketone emissions from stationary sources"
- EPA Method 8315A, "Determination of carbonyl compounds by high performance liquid chromatography (HPLC)

APPENDIX 5
SAMPLING AND ANALYSIS OF AMMONIA

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1. INTRODUCTION

This report presents the current sampling and analysis method used by Ramboll Analytics for ammonia emitting from the ducts and stacks in amine based post combustion capture processes (PCC).

2. SCOPE

The proposed method describes the sampling and analysis procedures of ammonia in monoethanolamine (MEA) based CCS-plant flue gas.

The method has been designed to measure ammonia concentrations at about 5 mg/m^{3}n in stationary source emissions.

The method is based on Japanese industrial standard (JIS K 0099:2004) on which the sampling is done into boric acid solution (5 g/L) and analysed with an ion chromatograph equipped with a conductivity detector.

Table 1. Scope of analytes

Compound	CAS-number	Max. MEA concentration the liquid sample	Detection limit µg/m^{3}n, sample volume 0,5 m^{3}n
Ammonia	7664-41-7	0,2 %*	5 000

3. NORMATIVE REFERENCES

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

Japanese industrial standard, JIS K 0099:2004: "Method for determination of ammonia in flue gas"
EN 13284-1:2001, Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method

EN 15259:2007, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report

EN ISO 3696:1995, Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)

4. ABBREVIATIONS AND TERMS

4.1 Abbreviations

AMP	2-Amino-2-methyl-1-propanol
DCM	Dichloromethane
DEA	Diethanolamine
DEN	Diethylamine
DL	Detection Limit
DMA	Dimethylamine
DNPIPA	N,N´-Dinitrosopiperazine
EA	Ethylamine
EDA	1,2-Diaminoethane
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometer
IDL	Instrument Detection Limit
LMW	Low Molecular Weight
MDEA	N-Methyldiethanolamine

MDL	Method Detection Limit
MEA	Monoethanolamine
MeOH	Methanol, methyl alcohol
MMA	Methylamine
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
MW	Molecular Weight
NDEA	N-Nitrosodiethylamine
NDELA	N-Nitrosodiethanolamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyridine
PCC	Post combustion CO_2-capture
RI	Refractive Index
SIM	Single-ion monitoring
SPE	Solid-Phase Extraction
T_b	Boiling point
TMA	Trimethylamine
UPLC	Ultra Performance Liquid Chromatography
UV	Ultraviolet
vis	Visible

4.2 Terms and definitions

4.2.1 Solvent amine(s)
Common name used in this study for alkanolamines.

4.2.2 Isokinetic sampling
Sampling at a flow rate such that the velocity and direction of the gas entering the sample nozzle are the same as the velocity and direction of the gas in the duct at the sampling point.

4.2.3 Analytical blank value
Value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all relevant reagents and materials.

4.2.4 Limit of detection (LOD)
Minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability.
The measurement value can be distinguished from the analytical blank value with a confidence of 99%, when the limit of detection is expressed as the mean analytical blank value plus three times the standard deviation of the analytical blank.
The limit of detection should preferably be calculated from the analytical blank. If this is not possible, the limit of detection can be calculated from the signal to noise ratio.

4.2.5 Limit of quantification (LOQ)
Limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus five to ten times the standard deviation of the analytical blank. The limit of quantification should preferably be calculated from the analytical blank. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio.

5. SAMPLING

5.1 Principle and minimum requirements

The test programme shall be established following the advice and requirements described in EN 15259:2007 (5.4, Clauses 6, 7 and 8).

Sampling should be carried out at one or several points in the sampling section, in accordance of the test of homogeneity carried out according the EN 15259.

Sampling is performed by using ambient temperature probe with a nozzle of know internal diameter, chilled condensate and absorption section, gas drying and sample gas volume measurements. A solid preservation chemical is added into condensate flask before sampling.

If sample gas will certainly not include drops, droplets or solid matter sampling may be performed as non-isokinetic sampling.

5.2 Sampling train and its operations

Principle of the sampling train is presented at the Figure 1.

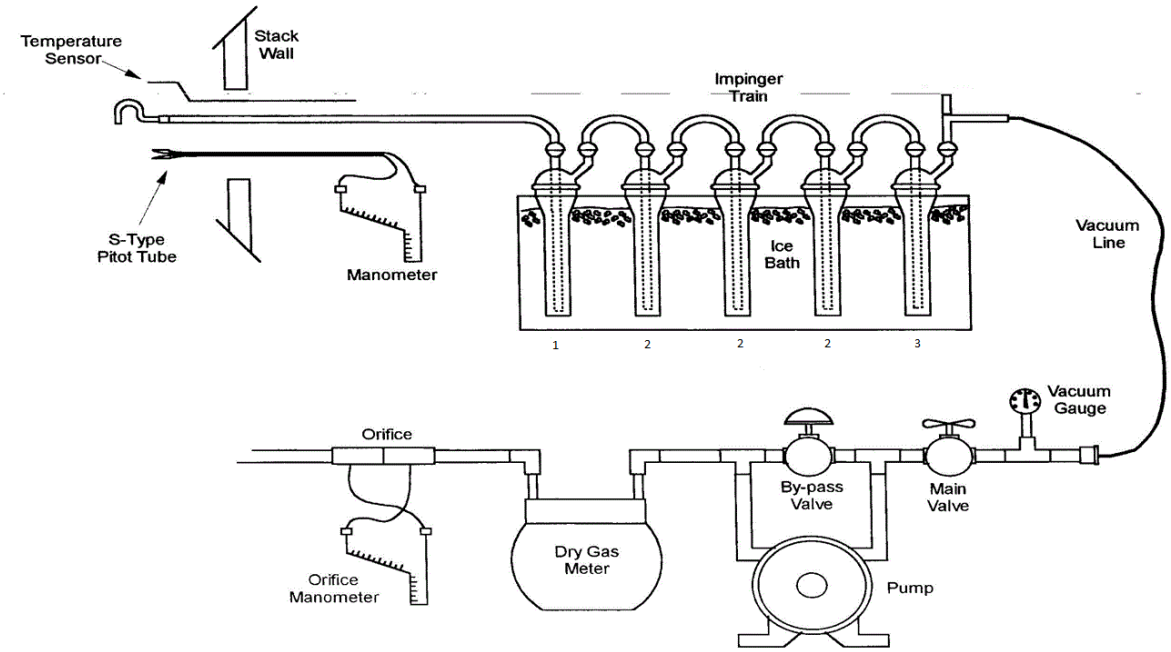


Figure 1. Principle of sampling arrangement, 1. condenser; 2. Absorbers; 3 silica gel

5.2.1 Probe

Unheated probe and entry nozzle without filter shall fulfil the requirements of EN 13284-1 excluding nozzle internal diameter which may be less than 6 mm. Nozzle i.d.'s less than 3.5 mm should be avoided. Area of nozzle entry should be specified in accuracy better than ±10 %.

Table 2 Evaluation of needed nozzle diameter at different flow gas velocities.

Nozzle size (diameter, mm)											
	sampling rate (l/min)										
Flow rate (m/s)	**0,2**	**0,5**	**1**	**2**	**4**	**6**	**8**	**10**	**12**	**16**	**20**
2	1,5	2,3	3,3	4,6	6,5	8,0	9,2	10,3	11,3	13,0	14,6
4	1,0	1,6	2,3	3,3	4,6	5,6	6,5	7,3	8,0	9,2	10,3
6	0,8	1,3	1,9	2,7	3,8	4,6	5,3	5,9	6,5	7,5	8,4
8	0,7	1,2	1,6	2,3	3,3	4,0	4,6	5,2	5,6	6,5	7,3
10	0,7	1,0	1,5	2,1	2,9	3,6	4,1	4,6	5,0	5,8	6,5
12	0,6	0,9	1,3	1,9	2,7	3,3	3,8	4,2	4,6	5,3	5,9
14	0,6	0,9	1,2	1,7	2,5	3,0	3,5	3,9	4,3	4,9	5,5
16	0,5	0,8	1,2	1,6	2,3	2,8	3,3	3,6	4,0	4,6	5,2
18	0,5	0,8	1,1	1,5	2,2	2,7	3,1	3,4	3,8	4,3	4,9
20	0,5	0,7	1,0	1,5	2,1	2,5	2,9	3,3	3,6	4,1	4,6

The probe should be about 0.5-1 meter longer than the diameter of duct. If two opposed sampling ports are available half of the duct diameter + 0.5- 1 m is adequate for the sampling probe

Accepted material of probe and nozzle is stainless steel (316 SS and 316l SS) or boron or quartz glass. Some minor parts as fitting and seals may be PTFE, otherwise it should be avoided. However, on very large ducts PTFE lines use may be necessary for the practical reasons, e.g.

when moving the probe inside the duct. On that case internal volume of PTFE tube should be minimized and number of blanks and washing practises evaluated. Internal diameter and length of probe should be minimized.

The probe may be marked before sampling in order to reach more easily the representative measurement point(s) in the measurement plane. It is important to specify the direction of nozzle entry.

If sampling is performed from the highly negative pressure duct, back flush from the absorbers into the duct is possible before and after the sampling sequence when pump is stopped. To avoid this, the connection between the probe and absorbers should be easily detached or suitable inert valve is recommended.

5.2.2 Condenser and absorber

To achieve an efficient absorption at least condenser and three absorbers shall be placed in series. Temperature of condensate flask and absorbers shall be cooled less that 5°C during the sampling.

On Condenser and absorbers the inner tube should reach the bottom of the impinger and end to bubble breaker or sintered frit to fine the bubbles.

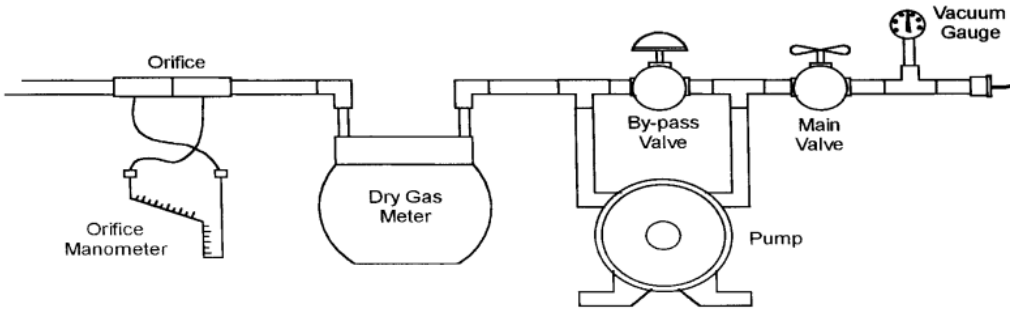
Recommended size of impingers should be capable of sampling on isokinetic flow rates without significant overflow of absorbent liquids. Recommended size of impingers is about 500 ml/impinger and absorber liquid volume of 300 ml. Condensate flasks may be bigger especially in high humidity and a long sampling periods. Extra protection bottle is recommended before silica gel.

When sampling hot gas or at warm conditions, extra cooler may be added before the condensate flask to avoid excessive break though of moisture from condensate flask into absorbers.

Absorption efficiency and carry out may be tested by analysing the last absorber separately. This may be hard to obtain for all analytes due to low concentration of analytes. In that case the analyte of highest concentration may be used for the evaluation, e.g. the main solvent amine. Breakthrough in the last bottle should not exceed 5 % from total amount.

5.2.3 Sampling pump

Leak-free pump capable of sampling gas at a set flow rate.
NOTE. A rotameter (optional) facilitates the adjustment of the nominal sampling flow rate.



5.2.4 Gas volume meter

Dry or wet gas volume meter may be used providing the volume is measured with a relative uncertainty of calibration not exceeding 2 % at actual conditions. The gas volume-meter shall be equipped with a temperature measuring device (uncertainty of calibration less than 2.5 K). The absolute pressure at the gas volume meter (uncertainty of calibration less than 1.0 %) can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10.5 °C or a volume content $\chi(H2O)$ = 1.25 %).

For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at 110 °C for at least 2 h.
When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

The relative pressure can be neglected if the gas volume meter is the last equipment of the sampling chain.

5.2.5 Sampling absorbent

Boric acid in UHQ-water (5 g/L) is used as an absorbent. The absorbent is made by diluting 5 g of boric acid into UHQ-water in volumetric flask and diluting to the final volume of 1000 mL.

5.3 Sampling procedure

5.3.1 Preparation and installation of equipment

5.3.1.1 Sampling location and sampling points

The sampling location is chosen according to EN 15259. A grid measurement is performed if homogeneity of sample gas is not validated.

5.3.2 Sampling procedure

5.3.2.1 Preparation

Homogeneity in the sampling plane should be evaluated before sampling as well as development of flow (direction, turbulence). Size and the arrangement of the duct shall be measured and recorded.

Required space is reserved before the sampling. Ice bath shall be cooled before the sampling. Rinse the sampling system prior to sampling by UHQ water.

Fill the absorbers at the clean area. Proposed amount of absorbent in the impinger is 60 % of the total volume, e.g. at 500 ml impinger recommended absorbent volume is 300 ml.

5.3.2.2 Checks

Check the velocities of flow at the sampling points, and calculate the sampling parameters to be achieved at each point (volume flow rate, sampling time), if required.

Ensure that the sampling train has been correctly assembled, and is leak tight, performing leak tests before each sample. Leak test shall be performed as below:

a) Assemble the complete sampling system, including absorbers
b) Seal the nozzle, or if not practicable, a connection between the condensate flask and probe air tightly.
c) Switch on the pump
d) Observe the rotameter / gas meter. Leak shall not exceed 2 % of the expected gas flow rate.
e) Release the seal SLOWLY and let under pressure disappear from the sampling system BEFORE turning pump off to avoid back flush of absorbers. Fast release of under pressure may break the bottom of flat glass absorbers.
f) Turn off the pump

5.3.2.3 Field blank

This procedure is used to ensure that no significant contamination has occurred during all the steps of the measurement.

A field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this report. This includes the sampling procedure without the suction step.

If the sampling system is in contact with the measured substance the system is cleaned and reused in the field, a field blank shall also be taken before each measurement series. The blank

taken after a measurement series may be used as the blank taken before the following measurement series.

The average sampling volume shall be used for calculation of the blank value expressed in µg/m^3n.

If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank.

Also sample from wash water, absorbent liquids on measurement should be stored as blank samples. These will be analysed if field blank shows unexpected positive concentrations.

5.3.2.4 Sampling

Taking into account the expected concentration related to analytical detection limit and flue gas flow, calculate the required sample volume and time. Suggested sampling rate depends on the design of the absorption flasks. In practice sampling rate of 5-7 l/min and sampling time of 0.5-2 hours are applicable.

Sampling procedure is as follows:

a) Record the gas meter values, temperature, pressure, startup time
b) Insert the probe in the duct. If sampling will not start immediately turn the nozzle pointing to the downstream of the flow before the sampling
c) Turn on the sampling pump
d) On the conditions of strong negative pressure, connect the absorbers and the probe open the valve between
e) Adjust the sample flow to required value
f) On grid measurement move the probe and adjust the flow rate accordingly without stopping the pumps
g) Maintain the temperature of ice-bath at required level
h) At the end of sampling, turn off the pump. On ducts of strong negative pressure disconnect the probe and absorbents before stopping the pump. At the end of sampling record the final gas meter readings
i) Wash the probe by following procedure, if possible,:
    a. Take the probe out from the duct
    b. Turn on the sampling pump
    c. Add UHQ water into the nozzle (about 10 ml) using washing bottle
    d. Let the water run to the condenser and stop the pump. Pump values on washing are not included the total sample amount!
    e. If the probes are impractical to take out of the duct between the sampling periods, in the case of negative pressure in the duct, add clean UHQ water from the absorber end of the probe to wash the probe.
j) Pour the condensate into the storage vessel. Plastic vessels may be used if sample is immediately frozen. Other cases glass vials with inert and air tight cap shall be used.
k) Pour the absorbent solvents excluding the last absorbent into the storage vessel. NOTE! The condensate and absorption liquids are not combined. Last absorption vessel shall be stored at separate vessel.
l) Wash the condensate flask by UHQ water and pour the washing into the storage vessel of condensate. Wash the absorbers respectively.

5.3.2.5 Storage of samples

Samples should be stored in cold. Frozen is recommended. Analysis should be performed as soon as possible.

6. SAMPLE PREPARATION

6.1 Principle

The determination of the ammonia is based on direct injection quantification with external standards using HPLC-CD with IC column.

6.2 Reagents and materials

6.2.1 Laboratory equipment

- Standard laboratory glassware such as Erlenmeyer flasks and beakers

- Balances with appropriate range and precision
- Pipettes
- Vials for sample extracts
- Millipore Milli-Q water cleaning system

6.2.2 Reagents

Solvents and reagents of sufficient purity shall be used, for example

- Boric acid (Merck, No. 1.00165.1000)
- Nitric acid (J.T. Baker 69.0-70.0 % or equivalent)

6.2.3 Standards

High purity standards shall be used, for example

- Ammonium chloride (Merck, No. 1.01145.0500 >99,8 %)

6.2.4 Internal standards (ISTD)

None

6.3 Procedure

The sampling absorbent is analysed with ion chromatography and quantified by method of external standard.

6.3.1 Blank sample

Blank sample will be treated and analyzed exactly as the actual samples.

6.3.2 Quality control

Standard addition to sample matrix will be done with each sample set. Recoveries will be monitored.

6.3.3 Pretreatment and cleaning

The sampling absorbent is transferred into a volumetric flask and the sampling container is washed with UHQ-water. The sample is diluted to known volume and an aliquot of it is placed into an LC-vial.

7. INSTRUMENTAL ANALYSIS

7.1 Instruments and chemicals

An HPLC-CD apparatus is used in ammonia analysis and the conditions are as followed:

- Column: Dionex IonPac CS14.4 x 250 mm
- Detector: Conductivity detector without a suppresser
- Column temperature: min. 65 ºC
- Eluent: Nitric acid 3 mM in UHQ-water
- Injection volume: 20 µL
- Isocratic conditions

IC or HPLC with a conductivity detector with a suppressor would be preferred but not tested during these tests. Also preferable column would be Dionex IonPac CS16.

7.2 Calibration

Reference stock solution of ammonium ion is prepared by diluting approximately 0.3 g dried ammonium chloride into a small volume of UHQ-water and diluting it into 100 mL with UHQ-water. The ammonium ion concentration in stock solution is roughly 1 g/L but exact concentration must be calculated. Standards are prepared by diluting the stock solution with suitable amounts of water. Typical standard concentrations are between 5-100 mg/L

7.3 Procedure

Analysis is performed with HPLC-CD against external standard calibration curve.

7.4 Quality assurance

Recoveries of standard additions and blank values are monitored.

8. RESULTS

8.1 Calculations

Results are calculated from peak areas from external standard calibration curve

8.2 Limit of quantification

LOQ is between 5 mg/L and 15 mg/L depending on the amount of near-eluting monoethanolamine in the sample.

8.2.1 Sample amount

$$Q_{analyte} = C \times V_s$$

$Q_{analyte}$	quantity of ammonia collected, in milligrams;
C	is the concentration of the solution in milligrams per millilitre;
V_s	is the volume of absorption solution in millilitres

8.2.2 Sample gas volume

For dry gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_{res}}{101{,}3}$$

For wet gas meter:

$$V_{std} = V_{T,\ p} \times \frac{273}{T} \times \frac{p - p_s(H_2O)}{101{,}3}$$

Where

V_{std}	the volume under standard conditions and dry basis, in cubic metres (m^3)
V_{Tp}	the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m^3);
T	Actual temperature in Kelvins
p	Total pressure in kPa at the gas meter
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);
P_{res}	is the residual vapour pressure, in kilopascals (kPa).

8.2.3 Final concentration

Final concentration in the flue gas is expressed as:

$$C_{analyte}\ [\mu g/m^3 n] = \frac{Q_{analyte}}{V_{std}}$$

8.3 Overall method uncertainty

As the method is based on direct injection, analytically the errors are derived from possible dilution steps, repeatability of the instrument and matrix effects. Instrument repeatability shall be resolved and multiple standard additions shall be done to actual sample matrix.

9. BIBLIOGRAPHY

Japanese industrial standard, JIS K 0099:2004: "Method for determination of ammonia in flue gas"