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#### ABSTRACT

The objectives of the project are described in the Tender Invitation of H&ETQPAmine1: "Establishing sampling and analytical procedures for potentially harmful components for post combustion amine based CO<sub>2</sub> capture". The present report covers Subtask 2: Procedures for manual Sampling, and covers sampling of amines, ammonia, aldehydes, amides, alkylamines, nitrosamines and nitramines.

The main challenges of manual sampling from a CO2-capture plant are: 1) the great number of possible compounds in the flue gas with widely varying physical properties, 2) the possible thermal instability and unwanted side reactions (generation of artefacts), and 3) the high water content of the emitted flue gas.

**Results/present status:** To our knowledge, no standardized manual sampling procedure exists, which is approved for the combination of the given compounds in flue gas. The methods available are primarily developed for ambient air measurements in the work atmosphere; thus low relative humidity and limited sampling temperature are prerequisites for application of these methods. Exceptions are procedures for absorption and derivatization of aldehydes in DNPH and the absorption of ammonia and amines in sulphuric acid. No single standardized sampling method exists for the broad spectrum of compounds given in the scope of work. As a consequence of this, the present status is that several sampling principles need to be utilized in parallel or series to collect all groups of components.

**Our recommended procedure** for manual sampling is a methodology based on cooling of the sampled gas followed by liquid analysis of the condensate and sampling and analysis of the dry gas after cooling by means of gas absorption solutions and adsorbents. The main advantage of this suggested procedure is that it avoids heating of the sampled gas thereby eluding unwanted thermally induced degradation and artefact formation and at the same time handles the challenge of high water content in the emitted gas, thus allowing the application of standardized methods used for manual sampling of ambient air on the dried gas downstream the condenser.

For future work, we suggest: 1) To perform lab scale experiments with a cold trap system in series with other absorption and adsorption systems. The lab-scale system will make it possible to perform studies of sampling efficiency and calculation of mass balance. The lab scale experiments will also allow studies with potentially harmful compounds as nitrosamines and nitramines. 2) To verify the lab scale experiments in the pilot scale VOCC test rig. The VOCC experiments will allow isokinetic sampling and controlled variation of a great number of parameters related to carbon capture chemistry and flue gas sampling.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Process Technology	Prosessteknikk
GROUP 2	Measurement	Måling
SELECTED BY AUTHOR	Flue Gas	Røykgass
	CO <sub>2</sub> -capture	CO <sub>2</sub> -innfanging
	Sampling	Prøvetaking



## **EXECUTIVE SUMMARY**

#### Objective

Manual emission monitoring on a  $CO_2$ -capture plant requires sampling methodologies combined with analyses which cope with the prevailing conditions (low flue gas temperature and high humidity) and expected low concentrations of trace components. The flue gas contains considerable amounts of water, further organic components like absorbents and their degradation products. The components to be analysed differ considerable in their physical properties, further thermal stability and side reactions are possible.

#### Status

To our knowledge, no manual sampling procedure which is standardized and approved for the combination of components and at given flue gas condition is available. Few components can be measured with standardized procedures, the majority can not be sampled and subsequently analysed with available methods. The methods available are primarily developed for ambient air measurements in the work atmosphere; thus low relative humidity and limited sampling temperature are prerequisite for application of these methods. Exceptions are procedures for absorption and derivatization of aldehydes in DNPH and the absorption of ammonia and amines in sulphuric acid.

Information with respect to the thermal stability of components is limited. However, thermal degradation of MEA has been reported in long sampling lines at elevated temperature ( $150^{\circ}$ C to ~ $180^{\circ}$ C) to avoid condensation, further formation of nitrosamines at elevated temperatures when nitrous oxide is present has been reported. Today's manual sampling systems are either operating at elevated temperature to avoid condensation or with cooled sampling probes. Heated systems are applied were a sample gas stream shall be divided into several parallel sampling units to ensure even concentration in all parallel trains. Cooled sampling systems are used for wet flue gases containing semi-volatile components.

The number of possible components in the flue gas with widely varying physical properties, possible thermal instability and unwanted side reactions (generation of artefacts) together with the high water content of the emitted gas sum up the main challenges of manual sampling on a  $CO_2$ -capture plant. No one single standardized sampling method exists for the broad spectrum of compounds. As a consequence of this, the present status is that complex batteries of sampling principles and equipment need to be utilized in parallel or series to collect all groups of components. This complexity gives both technical and practical challenges.

#### Recommended procedure for manual sampling

SINTEF proposes a procedure for manual sampling based on cooling of the sampled gas followed by liquid analysis of the condensate and sampling and analysis of the dry gas after cooling by means of gas absorption solutions and adsorbents. The main advantages with this suggested procedure is

- 1) Heating of the sampled gas is avoided, thus preventing unwanted degradation or artefact formation in the sample.
- 2) The procedure handles the challenge of high water content in the emitted gas

#### Suggested further work

Sampling procedures where the flue gas stream is dried in a knock-out condenser and/or subsequent refrigerated cold trap has potential as shown by the performed proof-of-concept at



SINTEF. Versatility of the system combined with high resolution analysis of the condensate phase by e.g. mass spectroscopy based instruments needs further verification.

Testing of the apparatus consisting of a knock-out condenser and/or knock-out condenser/refrigerated cold trap combination, with respect to efficient transfer of components from the flue gas to condensate phase is advised. The VOCC-test facility at SINTEF can be used to simulate wet flue gas from an absorber with possibility to include numerous absorbents or degradation products.

The following work is suggested:

- Optimization and testing of the efficiency of the proposed knock-out condenser. (Efficiency in terms of amount organic compounds removed from the flue gas stream at a given dry gas exit temperature e.g.: -10, 0, 4 and 20°C).
- Separate analysis of the condensate phase and the subsequent dry gas analysis in order to establish understanding of the split between phases.
- Evaluation of whether analysis of the condensate is sufficient for the total analysis of the compounds of interest. (It is expected that most of high boiling components will condense and therefore limited amount will be in the gas phase).

Application of liquid absorbents and/or solid adsorbents to the dried gas streams is straight forward, but research and development is necessary in order to implement the complete setup for our suggested sampling procedure; based on the suggested principle an evaluation of applicability, accuracy and efficiency could be completed within 6 month.

Practical implementation of the suggested work:

- Bench scale experiments where a complete control of the mass balance in a closed system which allows for assessment of the efficiency of the proposed sampling methodology.
- Bench scale experiments will also allow flue gases which contain components like nitrosamines and nitramines.
- After evaluation up-scaling and testing on SINTEF VOCC test facility will be performed.



## Abbreviations

AHMT	Alkaline method
AMS	Automated measuring system
BAT	Best Available Technology
BREF	Best Available Technology Reference Document
CSI	Chemical Sampling Information
EHS	Environmental Health Safety
FID	Flame-ionization detector
FTIR	Fourier transform infrared
GC	Gas chromatography
IPPC	Integrated Pollution Prevention and Control
IR	Infrared
LC	Liquid chromatography
LOD	Lower limit of detection
MCERTS	Environments Agency's Monitoring Certification Scheme (Great
	Britain)
MEA	Monoethanolamine
NDIR	Nondispersive infrared
NITC	1-naphthylisothiocyanate
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
RH	Relative Humidity; 100% = dew point @ given temperature
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
VOC	Volatile Organic Carbon
VOCC	Validation of Carbon Capture
2-HMP	2-(hydroxymethyl) piperidine



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## **1 INTRODUCTION**

#### 1.1 Background

The fundamental objective of the planned  $CO_2$  capture plants is to minimize the emission of  $CO_2$  and contaminants in the treated flue gas released to the atmosphere. For the qualitative and quantitative measurements of the emissions it is crucial to establish appropriate measurement sites, sampling procedures, analytical procedures and subsequently evaluate automated analysers and if possible online-monitoring system (i.e. an AMS – Automated Measuring System). The aim of the present subproject (H&E TQP Amine 1 Subtask 2) is to present "Procedures for manual sampling" from the sweet gas stream exiting the absorber and water wash section, respectively. Procedures shall be universal applicable for both pilot plant test and full scale.

Further details about the background of the project are given in the tender document H&ETQPAmine1: Attachment A1: "Scope of Service: Establish sampling and analytical procedures for potential harmful components from post combustion amine based CO<sub>2</sub> capture".

#### 1.2 Scope of work

In order to support Company in the performance of comprehensive emission measurements both for process operation and required by authorities) procedures for sampling are presented. Literature (international standards and guidelines) is reviewed and appropriate procedures evaluated with respect to applicability.

The objective of manual sampling requires considerable attention to take care of a series of subsequent considerations which arise:

- Manual sampling for analysis of gaseous and condensed components: The collection of samples, need to be designed in such a way that components are collected by appropriate absorbents or adsorbents for further processing. Collection can be performed in a series of generally cooled impingers where characteristics of the absorbents are tailored for given components. Regarding adsorbents, limitations for application regarding the upper limit for relative humidity of the gas sample should be considered.
- The sampling system and procedures shall not generate alternations (degradation or artefact formation) of the samples taken and allow for efficient sample handling considering valid HSE-requirements.
- High volume sampling for toxicology tests will require systems which are not dependent on adsorbents or absorbents which in itself will have adverse effects. Thus, the components from the flue gas shall neither be diluted nor mixed with other components which might have influence on the toxicology of the resulting mixture. Further, the samples need to be protected from other effects like UV or oxygen to avoid photocatalytic or oxidizing reactions.

The present study shall cover procedures for adequate sampling, sample treatment and storage for both pilot and full scale design of a  $CO_2$ -capture plant. Though information on these two systems is still limited, we assume that operation conditions are similar; the principal difference will be the emission cross section.

The lower limits of detections (LOD) of the different methods are strongly dependent on the combination of chosen sampling technology and the subsequent sample handling and analysis. Therefore the presented LOD (though scarce) are only indicative; improved analysis technology will easily improve LOD in the flue gas from mg/Nm<sup>3</sup> to  $\mu$ g/Nm3. The influence of improved analysis will be in depth treated in Subtask 4 /3/.

# **()** SINTEF

The role of Subtask 2 (Procedures for manual sampling) in the total sampling and analysis chain given through the individual subtasks 1 to 5 is presented in Table 1-1.

Sampling and analysis chain											
Stack	Measurement	Sampling	Component	Analysis							
	section	equipment	collection	Manu	al sampling	Online sampling					
Parameters:	Position of	Probe cooled or	Adsorbent (solid)	Samp	ole	Sample transfer					
Flow	section	heated	Absorbent (liquid)	pretre	eatment	to analyser					
Temperature	Number of		Condensation								
Humidity	access ports	Single or		Туре	of analysis	Type of analysis					
Concentration	Type of access	simultaneous	neous Sample		iment	instrument					
profile	ports	multi-	Preservation								
		component		Limit	of detection	Limit of					
		sampling				detection					
S	ubtask 1		Subtask 2		Subtask 3						
					Subtask 4						
					Subta	isk 5					

#### Table 1-1: Sampling and analysis chain

Appropriate placement of a measurement section and an initial presentation of sampling equipment is presented in *H&E TQP ID1: Subtask 1: Design of Sampling Points in treated flue gas* /1/. Online sampling will be presented in-depth in *H&E TQP ID1: Subtask 3: Online Sampling* /2/. Further there is overlap with *H&E TQP ID1: Subtask 4: Literature study* /3/. We also refer to previous work on performed on an initial evaluation of online sampling:  $CO_2$ -Kårstø – Concept study no. 9, selection of gas analyser and monitoring system/4/.

### 1.3 Report outline

Chapter 2 gives the basis for this study, which is mainly a summary of the information given by the Company combined with an overview on possible components formed through degradation of absorbents. The physical properties of the components are presented since these give the framework for sampling and analysis. Chapter 3 presents a brief overview over valid guidelines for sampling from stationary sources. In Chapter 4 sampling devices and procedures for the problem at hand are presented including their limitations. The procedures are discussed with respect to their applicability and necessary adaption for emission monitoring in wet flue gases. Conclusions, recommendations and necessary further work are presented in Chapter 6, 7 and 8, respectively.



## **2** BASIS FOR THE STUDY

The present objective requires considerable attention to take care of the rather specific and nonstandard components with respect to emission monitoring. Emission monitoring is a rather mature field according to IPPC's presentations (BREF and BAT documents) considering waste incineration and industrial (processing and cement) applications /5,6/. However, the components considered here are rather specific to amine based carbon capture and few to none standards for their manual sampling and analysis (off-line) are available. However, some of the components are regularly measured in ambient air (work atmosphere) /MCERTS 7/. Adaption of these methods to the present sampling task requires considerable attention since the gas matrices and conditions are fundamentally different.

Sampling procedures to be developed shall equally be applicable for manual sampling and high volume sampling for toxicity testing. Note that requirements for these two sampling purposes differ considerably.

Analysis shall be performed such that manual emission monitoring of the wet flue gas is performed. The sweet gas temperature is expected to be 25 - 50° C and contain components such as absorbents (e.g.: amines) and their degradation products; further water droplets from the water wash section are expected. It is not known a priori how much water soluble components are carried upwards between sections (absorber and wash sections) through entrainment. Further, most of the components of interest have a relatively high vapour pressure, thus adequate sampling of both gaseous and aerosol/liquid phase is essential. Flue gas components from a combustion process are expected, however these are not the topic of the present study; analytical methods are readily available and therefore presented only briefly. Manual sampling procedures need to consider:

- Gaseous and liquid samples with droplets (aerosols to large drops depending on the type of demister)
- High water concentration in the flue gas, the dew point and corresponding water concentration as function of temperature is shown in Figure 2-1. Little is known about the effective water concentration of the flue gas. Assuming addition of 1 droplet with 1.5 mm diameter per litre air results in an increase of 14 gram water per kg air.
- Insufficient knowledge with respect to thermal stability at elevated temperature of some components because of inconsistent literature.

For toxicity tests an adequate high volume sampling procedure needs development. Based on emission sampling the following additional requirements need consideration:

- Samples shall not degrade during sampling (heat sensitive) thus impose minimum change of components.
- No dilution of components.
- Avoiding sampling on solid adsorbents or liquid absorbent which by themself might have adverse environmental or toxic effects.

#### 2.1 Process design

The basic flowsheet of a  $CO_2$ -capture plant together with mark-up of a specific location of a measurement site is given in Figure 2-2; operational parameters for treated flue gas (sweet gas) are given in Table 2-1.



For simplicity, the description of the operation mode of a CO<sub>2</sub>-capture plant is omitted and we limit attention to the absorber system itself. Flue gas entering from the up-stream process will be cooled and enters the absorber from the bottom; flue gas will be distributed over the absorber packing material (potentially in several parallel sections) and get in contact with the absorbent (water-amine mixture). An average flue gas velocity (superficial) in the absorber of 2 - 3 m/s is suggested.



Figure 2-1: Relative humidity as function of temperature /8/

On top of the absorber section water wash sections will be installed to minimize emissions of amine and other possible hazardous components. Treated flue gas exiting from the wash sections will be transferred into an exit pipe placed on top of the absorber and wash section structure. The mechanical design of the stack (exit point) is not yet given and we therefore assume a circular cross section with a smooth transition from water wash section into the exit stack.



Figure 2-2: Simplified process diagram, circled part is focus of the study (SINTEF)



#### 2.2 Operational conditions

We assume that operational conditions (both with respect to flue gas components as well as flow conditions) in full scale and pilot will be kept as similar as possible. The flue gas conditions and composition, sweet gas (absorber outlet stream) conditions and composition, given here are based on information extracted from the document H&ETQPAmine1: Attachment A1 and given directly from Company. The treated flue gas from the stack will be saturated with water and the conditions and compositions are given in Table 2-1. The velocity in the exit pipe is estimated to 20 m/s (information from Company).

Conditions	Units	Nominal values Pilot scale	Nominal values Full scale			
Flow (Normal)	Sm <sup>3</sup> /h	250 - 1200	$0.72 - 2.3 * 10^{6}$			
Temperature (Normal)	°C	25	- 50			
Pressure (a)	bar	1.01	1325			
Main body velocity	m/s	2.0 -	- 3.0			
Exit velocity after water wash	m/s	20	20			
Composition						
Oxygen (O <sub>2</sub> )	wt-%	15				
Nitrogen (N <sub>2</sub> )	wt-%	80.7				
Carbon Dioxide (CO <sub>2</sub> )	wt-%	0.6				
Water (H <sub>2</sub> O)	wt-%	3.9				
NOx	ppm	?	$2 - 20^{+}$			
NH <sub>3</sub>	ppm	?	< 50			
$SO_2$	ppm	?	$0.10^{+}$			
Amines	ppmv	?	< 5			

Table 2-1. Rommal conditions and composition of theated flue gas (sweet gas
-----------------------------------------------------------------------------

#### 2.3 Components

A list of components to be sampled as well as their physical properties supplied by company are presented in Table A1- of Appendix 1, further we include information for other components and degradation products of piperazine, MEA, MDEA and AMP (H&E TQP ID4: *Protocol for evaluation of solvents – Process and atmospheric chemistry*) in Table A1-1 to A1-5. The boiling points of components presented in Table A1-1 to A1-5 are presented in Figure 2-3 were the boiling point of components is plotted versus an index for simplicity.





# Figure 2-3: Boiling point of components (X-axis: chronological component number from Tables A1-1 to A1-5 in Appendix 1)

The thermal stability of components and their boiling points together define a range of operation temperatures for sampling and analysis devices; too high temperatures result in decomposition of absorbents and potential artifact formation in the sample. On the contrary too low temperatures will lead to adsorption/absorption, condensation and deposition of components in the sampling transfer lines and analyzer system. All these effects will have negative influence on the analysis result and need consideration.

## **3** BACKGROUND ON SAMPLING FROM STATIONARY SOURCES

Flue gases in a stack may be inhomogeneous due to stratification or swirling caused by duct design and geometry. Therefore average concentrations and velocities at several evenly spaced measurement points across a measurement plane need to be determined. Measurements are performed as grid measurements over a measurement plane and several measurement planes should be used to identify the proper sampling location. Details on design of measurement section and measurement plane are treated in Subtask 1 /1/.

In the following we present general standards and guideline for the sampling itself (see Table 3-1). Note, we assume that the sampling is performed iso-kinetically for each component individually /1/.

Identifier	Title	Method / principle
EN 15259: 2008-1	Air quality. Measurement of stationary source emissions. Requirements for measurement sections and sites and for the measurement objective, plan and report	
VDI 4200: 2000	Realization of stationary source emission measurements	
ASTM 3154-00	Standard Test Method for Average Velocity in a Stack (Pitot Tube Method)	Differential pressure measurement; Pitot tube with micromanometer,
ISO 10780	Stationary source emissions – Measurement of velocity and volume flow rate of gas streams in ducts	Differential pressure measurement; Pitot or S-pitot tube with micromanometer, temperature compensation
ISO 3966 Annex A; 2008	Measurement of fluid flows in closed conduits – Velocity area method using Pitot Tubes	Differential pressure measurement; Pitot tube with micromanometer,

Table 3-1: Overview Guideline and Standards relevant for design of sampling system



## 4 MANUAL SAMPLING

The present chapter presents existing methods developed for sampling (absorption or adsorption) from stationary sources. The methods available are limited to classic flue gas components from combustion processes and methods for short chained aldehydes, alkylamines and amines. For the remaining components no approved procedures are found by the authors. However, extensive work has been performed to develop methods for analysis of air quality in the work environment. These methods /9/ are designed for sampling of ambient air, thus moderate temperatures and relative humidity are necessary for these methods to give correct results.

Emission measurements for regulatory purposes are performed according to guidelines given in international emission measurement standards /for example: 5,10,11 and 12/. If measurement standards exist for a certain exhaust gas component, accredited measurements can be performed of it by a certified measurement company (see Table 3-1 and APPENDIX 2 Table A2-1). If no international standard exist for a component, measurements can be performed according to national directives but will not be accredited.

Sampling of components from a stationary source (flue gas stream) requires adequate methods for each given component; for numerous components standards, specific procedures or guidelines are developed, a collection (and most probably only a fraction of what is available) is presented in Table 3-2. However for the components of interest few to none procedures are available for sampling from a stationary source, procedures are available for ambient air sampling (see Table A2-2) developed for work environments.

Sample collection can be performed by different types of equipment and collection of the components is performed in a series of generally cooled gas wash bottles or impingers, and different component groups are collected by appropriate absorbents (bases, acids, solvents) or adsorption tubes (solids, e.g.: activated carbon) for further processes (for detail see /1/).

For toxicity testing we may expect to include large sampling volumes, and absorbents cannot be used since non-destructed samples are needed for toxicity tests. Adsorbents may be used if nondestructive desorption is possible without affect on the original toxicity of the flue gas samples. Of specific interest are analysis of potential hazardous compounds, which primarily are organic compounds.

#### 4.1 Challenges

Sampling of the vast number of different components is challenging because of:

- Melting and boiling point range; which might lead to precipitation if the sample stream is heated.
- Insufficient (and partly contradictive) information regarding the thermal stability of some components.
- Insufficient information on the distribution of components between a gaseous and liquid phase (Vapor-Liquid Equilibrium).
- The sampling framework with a flue gas stream above dew point.
- For few to none of the organic components of interest sampling and analysis procedures for emission monitoring are established and verified.

In Chapter 4.2 we present sampling systems applicable for sampling at a CO<sub>2</sub>-capture plant. These designs need adaption through application of proper sampling devices for a given component or components groups taken care of gas matrix and conditions (see



Table A2-2). Particulate matter sampling is performed with filters as separation medium. Gaseous emissions are sampled with a sampling train of absorption flasks or solid adsorbents where the emissions are trapped.

In order to be able to compute emissions that are corrected to dry conditions, the moisture content in the flue gas has to be determined. If only the concentration of a certain flue gas component is of interest the flue gas flow does not have to be determined, otherwise the flow has to be measured in addition to the other parameters. All flue gas sampling has to be performed isokinetically to ensure that representative samples are collected.

#### 4.2 Existing standard configurations for manual sampling from stationary sources

For manual isokinetical sampling the principle design of a sampling system consists of a probe (inserted into the stack), some sampling device, a gas dryer, a gas meter and a vacuum pump combined with velocity meter and control unit. Further, temperature and pressure in the sampling system should be recorded. The vacuum pump generating suction from the stack is controlled by means of a velocity sensor in the stack (in general a pitot tube) to ensure iso-kinetically sampling. For operation of these systems (installation and set-up, leak testing, determination of sampling volume and velocity) we refer to appropriate standards presented in APPENDIX 2 Table A2-1.

#### 4.2.1 Single component sampling system

In Figure 4-1 a flowsheet for isokinetic sampling is presented, the systems can be applied for (complex) organic components which are either in gaseous, aerosol, liquid or solid state at the sampling point. The sampling can be performed either by "main stream (a)" or "side stream (b)" (also called "partial stream" sampling).



Figure 4-1: Isokinetic sampling system (Source: EN 14385:2004)



A particle filter (3) is placed either in front or behind the sampling probe. This renders necessary heating of the filter in order to fully evaporate the sampled gas passing through the filter.

The sample gas stream from the stack is then either passed through absorbent filled gas wash bottles (9; multiple impingers in series) to remove gaseous components or aerosols, the gas stream is dried (4) and the dried gas stream registered (10). The combined concentration of a component is determined through analysis of the filter and the wash bottle content.

Alternatively in the side stream method, a smaller stream is split from the main stream and passes through a series of absorbent filled wash bottles. Pre-requisite for a split of the gas stream is that the sample gas stream is "gas only" (no droplets, particles)

The choice which of the two methods are preferred is often dependent on the gas conditions (e.g. wet gas would dilute the absorbent; therefore = side stream) or on the combination of component concentration and limit of detection (low concentration = Main stream). In addition, a side stream setup is necessary in order to fulfil the optimal gas flow requirements for impingers and adsorption tubes.

#### 4.2.2 Multiple component sampling system

For simplification of sampling of multiple components from a gas stream, the splitting of the extracted gas stream is frequently applied /13/, the system design is shown in Figure 4-2 which is an extension of the side stream system presented in Figure 4-1. The adequate splitting of the isokinetically withdrawn gas stream is straight forward, provided a low dust load is ensured and that all constituents (aerosols and droplets) of the entire gas stream are evaporated properly.

The system is designed such that a main vacuum pump maintains an iso-kinetically withdrawn sample gas stream from the stack, the gas stream is dried and the volume flow registered. The flue gas is heated up to a temperature above boiling point of the highest boiling component (rule of thumb for waste incineration  $150^{\circ}$ C), passes over a particle filter (dust, salts) and enters a gas splitter. Provided the temperature of the entire gas stream is <u>above the dew point for the individual components</u> a split of the gas stream can be performed. Each individual sampling train can now be optimized for a given component; each sample train needs also individual gas pumps and gas metering to ensure proper analysis and back-calculation to the gas stream conditions. The gas flow of the main pump is adjusted for the gas flows of the individual absorption / adsorption systems 1 - 4.

The individual absorption / adsorption units 1 - 4 for collection of components can be chosen from a variety of alternatives, ranging from cooled impingers, liquid filled gas wash bottles or thermal adsorption tubes. The heated flue gas exiting the heated splitter needs to be properly conditioned to ensure that the chosen collector function properly.

Please note:

- The application of this design requires in-depth knowledge of the expected components, their precipitation / boiling / dew point in the given gas matrix and information regarding the thermal stability of individual components.
- A too high temperature in the evaporator unit might lead to unwanted decomposition of thermal unstable components. Formation of thermal degradation products of amine has been reported for systems with elevated temperature (above 150°C) and longer residence times because of long sampling lines (11/min and 50m) /14/. Further, induced artefact formation of e.g. nitrosamines is possible if nitric oxide or nitrogen dioxide are present /15/.



- Failure to evaporate all components (lack of residence time or to low temperature) will result most probably in an uneven split of the stream.
- Verification that the filter upstream the splitter does not contain considerable amount of dust is required such that components with high boiling point are not adsorbed on the surface of particles.
- For gases with high boiling components or where components precipitate, the application of the system is questionable since a proper collection of matter on the filter is not ensured.
- The authors didn't find literature on the efficiency of the given arrangement in Figure 4-2; it is not a standardized method, however, the system is widely used for emission monitoring applications to reduce time consumption for sampling /13/.



# Figure 4-2: Extractive manual simultaneous sampling of several components by gas stream splitting /13/

Multi-component sampling can be performed with a set-up according to Figure 4-2 for flue gases with negligible dust concentration and moderate humidity. Standard absorption methods for flue components like H<sub>2</sub>O, HCl, SO<sub>2</sub> etc. are presented in APPENDIX 2

Table A2-1. Flow velocity measurements are performed with standardised L-type pitot tubes according to ISO 3966:2008 to ensure isokinetical sampling. The flue gas is drawn through a heated sampling probe, passes over a filter to remove particulate matter and then enters two chilled gas wash bottles in series. The gas wash bottles are filled with a solution of 1 M  $H_2SO_4$  for absorption NH<sub>3</sub> and 3%  $H_2O_2$  for SO<sub>2</sub>. Analysis can be performed by means of ion chromatography (IC).

The standards EN 1948, parts 1 to 3 describe sampling, extraction/recovery and analyses of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and polyaromatic hydrocarbons. The samples are collected isokinetically by means of a cooled sampling probe (for apparatus see , top) glass fibre and a solid adsorbents (XAD-2).



The VDI 3862 consist of a series of 7 Guidelines for sampling and analyses of aldehydes, either as total aldehydes /ketones or as individual components. The components in flue gas samples may be specifically converted to target analytes which can be directly analysed to high specificity (e.g. VDI 3862).

Filter materials and solid sorbents used for sampling organic components are extracted in solvents for concentration and analyses of organic components (e.g. diethylether/n-hexane or other solvents). Condensates are extracted with n-hexane, samples are then concentrated before analysis according to e.g. ISO11338-2:2003 /16/.

Sampling of alkylamines and amines can be performed by absorption in sulphuric acid ( $H_2SO_4$ ). The flue gas is drawn through a heated sampling probe, passes over a filter to remove particulate matter and then enters two chilled gas wash bottles in series to avoid breakthrough because of saturation of the absorption solution. The gas wash bottles are filled with a solution of 1 M  $H_2SO_4$  for absorption.

#### 4.3 Sampling system proposed by SINTEF for wet flue gases from CO<sub>2</sub>-absorber

Sampling systems described in chapters 4.2.1 and 4.2.2 are applicable for flue gases with low water load, otherwise either liquid absorption units or solid adsorbent units will accumulate condensed water. In both cases efficiency will decrease with increase of humidity (dilution and water coating of surface, respectively). For sampling problems which encounter the following issues: high water concentrations (ensuring evaporation is difficult), precipitating components, components with high boiling points or thermal unstable components; these systems should not be applied. Instead of attempting transfer of the entire sample stream into a homogeneous gas stream by excessive heating and split into individual streams before sampling, we propose to remove particles and condensable in a cooled unit (see Figure 4-3) prior to splitting of the gas stream. A similar scheme is applied for sampling of PCDD/PCDF described in EN 1948-1 /17/. The removal of condensable and particulate matter in a knock-out condenser converts the gas stream into a "clean" and dried gas stream which readily can be divided.

### 4.3.1 Optimized sampling by condensation of flue gas stream

SINTEF propose the design of a flue gas sampling system optimized for sampling in wet flue gases with volatile and semi-volatile flue gas components. The system consists of a cooled sampling probe and a knock-out condenser with demister on the gas outlet. Condensate is collected in the bottom of the condenser drum and can be collected for analysis. The dried flue gas (dew point e.g.: 4°C) can be subjected to several sampling trains in parallel. One main stream is withdrawn to ensure isokinetic sampling.

After removal of condensate the flue gas can be treated in numerous different ways. These are:

- Split into different parallel trains for individual sampling of components in dedicated sampling units.
- Pass through absorption solutions without the possibility of dilution of the absorbent through humidity from flue gas.
- Pass over absorption tubes for interior environment measurements for components where appropriate flue gas sampling methods are not available. Interior environment measurements are in general restricted to gases with a low relative humidity<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> According to OSHA analysis of Nitrosamine Mixtures (OSHA method 27) is performed with Thermosorb N tubes for sampling at 22°C and 80% relative humidity.



The determination of individual components requires analysis of both the liquid phase and the absorption unit. The initial cooling unit can be either a standard cooler with process water as coolant or a refrigerated cooler to remove components with lower boiling points. The operation is analogue to the system presented in chapter 4.2.2, the individual sampling legs are adjusted to an appropriate sample flow (e.g.: impingers with absorption solutions 2 l/min and 0.2 l/min for activated carbon tubes). A flow controller can be utilized to ensure isokinetically withdrawal from the stack by adjustment of the main pump. Registration of all gas flows through the system allows computation of the flue gas concentrations.



Figure 4-3: Recommended sampling system for wet flue gases

#### 4.3.2 Proof-of-Concept: Cold trap

An extension of the scheme presented in Figure 4-3 is the replacement of the knock-out condenser by a solution where the gas stream passes through a cold trap at low temperatures (see Figure 4-4). The cold trap is in principle a refrigerated knock-out condenser. Initial test performed at SINTEF where an impinger is surrounded by a cooling medium at temperatures of -20°C (see Table 4-1) and -75°C (see Table 4-2) showed that flue gas components with a boiling point range ranging from - 10°C upwards can be trapped. The volatile compounds studied were ammonia and the alkylamines; methylamine, ethylamine and dimethylamine. The performed experiments are proof-of-concept towards a high volume sampling system without utilization of liquid or solid absorbents.

#### Experimental

The test mixture consisted of 1 mg/mL of ammonia and 10  $\mu$ g/mL of each of the alkylamines methylamine, ethylamine and dimethylamine. Cold trapping was performed in an empty gas washing bottle at -20°C and -75°C. A midget impinger with 20 mL 0.1 N H<sub>2</sub>SO<sub>4</sub> absorption solution



was mounted after the cold trap in a sampling train for collection of non-condensed components. The concentrations of amines were analyzed in the water trapped in the cold trap and in the absorption solution by GC-MS after derivatization. The total amounts of amine were calculated in the trapped water and the absorption solution.



#### Figure 4-4: Cold trap experimental set-up

#### **Initial results**

#### Table 4-1: Experiment performed at -20 °C

Analyte	Amount in cold trap (percent)	Amount in absorption solution (percent)
Ammonia	16	84
Methylamine	60	40
Ethylamine	54	46
Dimethylamine	64	36

#### Table 4-2: Experiment performed at -75 °C

Analyte	Amount in cold trap	Amount in absorption solution				
	(percent)	(percent)				
Ammonia	71	29				
Methylamine	92	8				
Ethylamine	85	15				
Dimethylamine	92	8				

#### **Initial conclusions**

The main conclusions are that:

- The most volatile amines (ammonia and alkylamines) can be trapped by a cold trap.
- Alkylamines are trapped more efficiently than ammonia.



• The relative amount of ammonia and alkylamines trapped in the cold trap is increased with decreasing temperature.

However, it is pre-mature to estimate the efficiency of the system based on these initial (though encouraging) experiments, because we assume that components are evaporated completely from the evaporator and that the final absorption in aqueous  $H_2SO_4$ -solution is 100% efficient. No amines were detected by the FT-IR-analyser, thus we assume that the efficiency of the acidic absorption is good, but we have not yet verified the applicability of the FT-IR for very low concentrations. It should also be noted that this applied setup using an impinger or gas wash bottle as cold trap has a significant potential for optimization regarding the design of the cold trap itself, as impingers and gas wash bottles have relatively low residence time of the gas and a low specific surface area.

# 4.4 Methods for sampling from stationary source emissions adapted from ambient air sampling

Additional methods of relevance for analyses of target components can be adapted from work on interior / work environment measurements, methods include sampling for analyses of ammonia, amides, alkylamines, nitrosamines and amines. All compound groups required the use of absorbents or solid adsorbents /18/ with subsequent solvent desorption, a summary of these methods are presented in Table A2-2. Numerous methods are given in the documentation provides by publications given by National Institute for Occupational Safety and Health /19/ and United States Department of Labour, Occupational safety and Health Administration /20/<sup>2</sup>.

The adaption of these sampling methods for work environment to emission monitoring on a stationary source is possible by application of the sampling equipment presented in Figure 4-3:

- Flue gas is withdrawn isokinetically from the stack by means of a cooled sampling probe.
- The sample stream is passed to a cooler which reduces exit gas temperature to at least 4°C.
- The dried gas stream can be divided into individual flows which are subjected to either liquid absorption or solid adsorption. Two sampling tubes are necessary to avoid saturation effects of the absorbent. According to EN 13649, there should be less than 5% of component in the second adsorption tube for a proper performed sampling.
- A purge stream passes through an empty chilled wash bottle and silica gel tower for drying of the gas, this stream is used to adjust the sampling volume flow to iso-kinetical conditions.
- Sample volumes and velocities are indicated in
- Table A2-2.

For a comprehensive analysis it will be mandatory to analyse both the condensate phase and extract from the absorption tubes; further register gas volumes in individual sampling trains and total gas volume. For desorption from the tubes in general extraction with some organic solvent, from condensate phase liquid-liquid extraction might be necessary. Combining both phases by some

<sup>&</sup>lt;sup>2</sup> Note these procedures are developed primarily for adsorption of components on solid absorbents at ambient conditions (low relative humidity @  $20^{\circ}$ C) in the work environment (for example: Dräger "Amin-Test"; operation range 10-40°C; Humidity 3-15 mg/l air corresponds to maximum 30% RH; interference with other alkalines is possible). Further, application of these methods to flue gas monitoring is not possible without adaption; because if the adsorption tubes are subjected to conditions where, part of the gas stream is condensing (e.g.: water when temperature falls below dew point) will lead to excessive flooding of the absorbent, thus reduce the adsorption efficiency considerably.



procedure for concentration of analytes and than analysis by means of e.g. HPLC or GC-MS is necessary.

From a sampling point of view it is straight forward to accumulate a liquid phase sample from a wet flue gas through by isokinetically sampling and cooling of the gas stream to condense components. However, this method will primarily collect higher boiling components (dependent on the cooling medium temperature, residence time and cooler design); while components with very low boiling points (e.g.: NH<sub>3</sub>, alkylamines) will be collected in the liquid phase only close to their equilibrium concentration determined by individual vapor-liquid equilibria. Some of these components will be present in a lower concentration in the sample compared to the real flue gas concentration (which is sum of component in gas and liquid phase at given conditions). The collection of components is a direct function of the temperature of the cooling medium; thus utilization of a sequence of a knock-out-condenser and a refrigerated cold trap with temperature in the order of -20°C might be necessary. Verification is necessary with respect to condensation temperature to ensure an appropriate sample composition.

#### 4.5 Operation manual for manual sampling

Manual sampling from stationary sources is standardized in numerous international standards; the most relevant are presented in Table 3-1.

Equipment for manual sampling for the given case is not more complicated or requires more space compared to traditional emission monitoring equipment. Standards with respect to design of a measurement site (e.g.: DIN 15259) define the design, size and capacity of necessary working platform to accommodate equipment for emission monitoring.

The operation manual is based on application of the Transportable Particle Sampling system from (Environnement GmbH, Germany). The system is applicable for sampling in wet flue gases and versatile enough to connect various sampling trains like: sampling gaseous compounds in adsorption solutions, filters and solid adsorbents. The TPS-system has been used in experimental studies in-house at SINTEF, and in on-site samplings. The individual units of the system are depicted Figure 4-5.

**Preparation of system**: Ahead of installation the entire system i assembled and leak tested. Tightening the sample nozzle by a blind plugg and starting the gas pump should result in a pressure of 0.5 bara. In other case the system needs inspection with respect to leakage.

**Installation of system**: selection of an appropriate measurement section is presented in Subtask 1 /1/. The cooled probe consisting of a Prandtl-tube, a thermocouple and the nozzle (EN13284 /21/) is installed in the stack. It is mandatory that the opening of Prandtl-tube and nozzle points directly countercurrent to the main body in the flue gas stream. Verification of positioning is necessary.

**Operation of system:** The sampling units (here impingers) are prepared according to the component to be samples. The gas pump and control unit are started and isokinetical sampling is performed for a given time. Sampling time is dependent on the combination of expected concentration of a component in the flue gas and the intended analysis instrument and its lower limit of detection.

**Data collection:** For appropriate sampling, total gas volume flow, temperature and condensate volume are registered. Samples taken in absorption solutions are transferred to analysis.









Suction tube with filter device, mounted at the probe. The filter device can be exchanged by a knock-out condenser. Gas trasfer to impinger bottles.



Drying tower, flowmeter and gas meter



Gas tight pump can set in front of the gasmeter.



Gas Cooler with Water Separator



Control unit for isokinetical sampling

#### Figure 4-5: Manual sampling system for wet flue gas

#### 4.6 Limits of detection

Limits of detection of a given sampling procedure is strongly dependent on how sampling is performed (e.g.: efficiencies of absorption / adsorption), the sample pretreatment before analysis (e.g.: desorption) and further the type of instrument which is applied for the analysis of key importance.

Procedure for classical flue gas components (NH<sub>3</sub>, SO<sub>2</sub>) achieve limit of detections in the order of  $10 - 100 \mu g$ /sample with ion chromatogarphy. Organic components like PCDD/PCDF have a lower detection of 1-5 pg/m<sup>3</sup> flue gas for individual congeners, provided appropriate sample preparation and analysis by GC/MS. More information on limits of detection is given in Subtask 4 /3/.

Sampling of alkylamine and amines by means of absorption in aqueous solution of sulphuric acid is possible. However, limit of detections of this procedure were not found in literature. Evaluation of work environment methods found in literature give widely varying information regarding the achievable lower limit of detection (LOD) or quantification limit (see Table A2-2). Further, it needs to be verified if these methods are applicable for emission monitoring, provided the adaption with respect to ensure relative humidity below dew point described above are performed. Limit of detections for e.g.: adsorption of Nitrosamine on ThermoSorb N provided by NIOSH<sup>3</sup> are in the order of 0.5 to 160  $\mu$ g/Nm<sup>3</sup> for dry air. Estimation of a combined limit of detection from analysis of liquid phase and adsorption on activated coal is not possible with current state of knowledge of the distribution of components between gas phase and liquid phase. Further discussion of limit of detection are performed in Subtask 4.

<sup>&</sup>lt;sup>3</sup> Note. ThermoSorb N can not be applied for applications with condensing humidity. Water on the adsorbent surface will inhibit adsorption of components, thus a to low concentration is found.



Even though sampling methods are developed for ambient air analysis (e.g.: determination of trace amounts of components in the work environment); some of these methods might be adapted to emission monitoring since they are based on impregnation of activated carbon with some agent. One particular example is the adsorption of ethylendiamine on with 1-Naphthylisothiocyanate /22/ (NIT) coated adsorbent tubes. The amines are derivatized to 1-Naphthylisothiourea which is directly analysed by HPLC. The method is originally developed from absorption of primary aliphatic monoamines in air by means of impinger trains, thus applying the original set-up is straight forward, the influence of water which condensates in the impinger need careful attention regarding dilution of the absorbent which will be detrimental for absorption.

#### 4.7 Preservation of samples

Sample preservation is challenging because of limited knowledge about interference between individual components and, degradation because of UV (degradation because of natural radiation) and exposure to air. Therefore, preservation of samples which are not derivatized (DNPH and NIT methods) requires special care. The following procedures are appropriate:

- Sampling performed through absorption in liquid solution requires air and liquid tight sealing of containers. Storage in refrigerated environment protected from UV-light.
- Sampling dedicated for components with low boiling points and high vapour pressure. Storing should be performed in freezers (<-20°C).
- Sampling performed on solid absorbents (ambient air / environmental methods) require that sample tubes are tightly locked, stored at low temperatures (refrigerator) and not subjected to sunlight.
- Long term storage of samples should be performed in freezers; temperature should be considerably lower than boiling point of NH<sub>3</sub>. (-33°C)

Stored according to procedures above, analysis shall be performed within one week from sampling. Disruption of especially cooling of samples has to be avoided. These considerations are "worst case" scenarios and need further verification.

*Sample preparation* on the laboratory would typically comprise any handling of samples between storing and the instrumental analysis. The two main purposes of the sample preparation are *cleanup* (removal of contaminants) to improve the performance of the instrumental analysis and *concentrating* to improve the sensitivity of the analysis.

During sample preparation, the *temperature* of the sample should be kept low whenever possible and exposure to *light* should be minimized. In addition, the sample preparation procedures should be minimized regarding the number of steps / duration of the procedure. If possible, the sample should not be exposed to extreme pH conditions or other strong reagents that may interfere with the result of the analysis.

If possible, extractions should be avoided, and dilution or direct injection is preferable because it gives minimal interference with the sample and also is a very simple and cost-effective way to prepare a large number of samples.

In some cases, extra care needs to be taken to avoid unwanted chemical reactions during sample preparation. A relevant example is the possible reaction between nitrite and secondary amines that forms nitrosamines as an artefact.



It must be controlled and verified that no degradation or unwanted chemical reactions takes place during the whole sample preparation process and on the autosampler and during instrumental analysis.

#### 4.8 High volume sampling for toxicology test

The basis for the sampling strategy is to collect cleaned gas removed from the absorber and use these samples for selected toxicity tests. This will require manual sampling combined with one or more methods for sample conservation before toxicity testing. The sampling method should be able to collect representative emission extracts containing gaseous, liquid phases and aerosols/particulates. The complete emission (including entrained droplets and evaporated substances) and compound groups of interest are primarily amines, ammonia, aldehydes, amides, alkylamines, nitrosamines and nitramines, with specific focus on alkylamines, nitrosamines and nitramines. Due to low concentrations of these compounds, large sampling volumes may be needed.

Sampling for toxicology tests require that the samples removed from the absorber are not altered through chemicals or absorbents which might have influence on the tests itself. The most promising design is presented in Figure 4-3; it is expected that a water rich phase will be sampled where components are presented in highly diluted concentrations.

From a sampling point of view it is straight forward to accumulate larger amounts of liquid phase from the flue gas by isokinetically sampling and cooling of the gas stream to condense components. However, this method will primarily collect higher boiling components (dependent on the cooling medium temperature, residence time and cooler design); while components with very low boiling points (e.g.: NH<sub>3</sub>, alkylamines) will be collected in the liquid phase only close to their equilibrium concentration determined by individual vapor-liquid equilibria. Thus, some of these components will be present in a lower concentration in the sample compared to the real flue gas concentration (which is sum of component in gas and liquid phase at given conditions). The collection of components is a direct function of the temperature of the cooling medium; thus utilization of a sequence of a knock-out-condenser and a refrigerated cold trap with temperature in the order of -20°C is proposed. Application of absorption units to improve efficiency is not possible since extraction of components from the absorbent in general is performed by organic solvents which are toxic itself.

#### 4.9 The measurement objective and the challenges

However, the number of "unknowns" involved in the sampling problem of flue gas from a  $CO_2$ -capture plant is considerable, thus development of a successful sampling strategy depends on indepth knowledge of:

- What and where to sample?
- How long to sample (including number of parallels) necessary to establish statistically valid results?
- Sampling conditions and gas matrix composition?
- Which sampling technique / method and what equipment is most reliable?
- Which analysis method allows for proper detection?

Further aspects like HSE, quality assurance and control; collection, interpretation and reporting of data need consideration.

In the present case the gas conditions and matrix is not well described and sampling of components needs consideration:



- Components are present simultaneously in different phases (gas, liquid (droplets / aerosols) and particulate matter (salts)); therefore the monitoring method needs to be able to sample the present phases simultaneously and appropriately.
- There is a need for a definition regarding analysis of the total amount of a component group (analogue to TOC) or speciated measurements; e.g.: alkylamines versus methylamine / ethylamine.
- Sampling time:
  - A suitable averaging period is strongly influenced by the short-term variation in emission levels.
  - Is it of interest to have the short-term variation (minimum and maximum emissions) or is an average over an extended time more appropriate?
  - The combination of sampling method and gas condition has influence on the maximum sampling time.
- The number of parallels and duration of the sampling needs to be determined to ensure representative data
- Field blanks are needed to determine the background, further they ensure that no contamination of the sample material occurred during sample handling and transfer
- The lower limit of detection of the analysis method / instrument and the percent uncertainty need evaluation. Note, efficiency of absorption and desorption needs to be considered when the sampling time is evaluated.

For components where no standards for sampling and analysis are established, thorough and comprehensive method development needs to be performed.



### **5 DISCUSSION**

The relevant constituents in flue gas belong to a broad spectrum of chemical classes ranging from bases to acids with a large variation in physical properties. No single standardized sampling method exists for such a broad spectrum of compounds. As a consequence of this, the present status is that complex batteries of sampling principles and equipment need to be utilized in parallel or series to collect all groups of components. This complexity gives both technical and practical challenges.

Further it is not obvious which components (see Table A1-1 to Table A1-5) and in which concentration they will be transferred from the absorber into the water wash and then released to atmosphere in either gaseous, aerosol or liquid droplets. The emission of droplets should efficiently be minimized by demisters installed downstream the water wash, however, aerosols of sizes less than 10  $\mu$ m are expected. Estimation of the amount of aerosol is outside the scope of this report; we refer to H&ETQP *Amine 6: Emission Reducing Technologies* /23/ for further details.

For regulatory required measurements of "classic" emission known from other industries like refineries, waste incineration and process industries development of measurement methodologies and sampling procedures is limited. Emission monitoring is generally well defined by standards (that means the components in question are defined in a permit) and necessary sampling and analytical procedures are standardized.

#### 5.1 Traditional flue gas sampling

The limited knowledge of the gas matrix requires attention to ensure a representative sampling; therefore iso-kinetically sampling is mandatory. Flue gas sampling procedures developed for sampling at stationary sources are well established. The extension of these methods to the component group to be analysed here is not straight forward, this is partly because of widely differing physical properties of the component (boiling point, thermal stability, reactivity) and they are present in different phases.

#### Traditional systems like these presented in

Figure 4-1and Figure 4-2 applied to simultaneous sampling of multiple components rely on heating of the sample stream prior to splitting of the stream. For most of the components in question few standardized methods exists for sampling from a wet flue gas stream. Existing methods are available for absorption and derivatization of aldehydes in DNPH; further absorption of ammonia and amines in  $H_2SO_4$  is well established. Limited information was found on limit of detections of these methods for the component groups.

Some of the components that are important to control in flue gas emissions have high boiling points (semivolatiles). These components may also be constituents of flue gas e.g. due to entrainment. The boiling points of components are presented in Figure 2-3 were the boiling point of components is plotted versus their chronological order from Tabels A1-1 to A1-5. The nitrosamines (see Table A1-1 to Table A1-5) are examples of compounds with boiling points from 150 to well above 200°C. In a standardized sampling approach one would normally need to heat the sampling lines to ensure that compounds with high boiling point not are deposited within the sampling lines or elsewhere within the system before they reach the adsorbent solution/tube. However, as indicated boiling temperatures of some components are considerable higher than 150°C which is a standard temperature for heated sampling equipment and also instrumentation. There is a substantial risk that some components will decompose if they are heated above 150 °C, either through direct heat or through increased reaction (partial combustion or oxidation) with other components. On the other hand formation of degradation products (e.g.: reaction of amines and NO<sub>x</sub>) will be possible if components are exposed to elevated temperature.



#### 5.2 Recommended sampling procedure and sample collection

Two common properties of the components present in the flue gas are that they are *water soluble* (polar) and *volatile* (low molecular weight and low boiling point), further there is the possibility of numerous components with very high boiling points. It was early indicated, that many water soluble compounds could be trapped together with water in a condensation trap, but it was not known whether the most volatile compounds could be trapped by condensation (see Figure 4-3 and Figure 4-4). Further, as a consequence of the possible thermal instability and high boiling points of components, and consequently the limited possibility to heat sampling lines, condensation (cold trapping) seems to be an adequate way to trap non-volatile or semi-volatile flue gas compounds without risk of thermal decomposition or generation of artefacts. *Therefore, a manual sampling system based upon a modified/optimized cooled sampling system is proposed. The system generates a condensate phase and a dried flue gas which is subjected to adsorbent media connected downstream in the sampling train. The knock-out condenser or cold trap section needs to be optimized to give a maximal and controlled trapping efficiency. However, it seems to be a promising concept (see Figure 4-3).* 

The results from a concept study with a refrigerated impinger performed at SINTEF showed that even the most volatile compounds (the alkylamines and ammonia) were trapped in the cold trap concept experiments. This result strongly supports the possibility of using a knock-out condenser combined with a cold trap sampling also for the more volatile compounds. However, confirmation of efficiency is needed.

#### 5.3 Limit of detection

The limit of detections of the individual sampling systems depends strongly on the type of components, type of absorbent / adsorbent, the principle of sample treatment (e.g.: adsorption and desorption of organics on activated carbon) and the type of analysis instrument involved. Sample handling (e.g.: freezing after sampling to avoid side reactions), derivatization of components (e.g.: aldehydes in DNPH) and sample transfer from collection site to analysis influence the quality of the analysis. The time of sample collection in a given absorbent or on the surface of adsorbents determines often the achievable lower limit of detection. Additionally, refereeing to the vast number of components which might be present, little to nothing is known regarding their interferences during analysis of the collected sample.

For the here presented (most probably incomplete collection of procedures) it is close to impossible to determine the limit of detections (see Subtask 4/3/ for more information), however, where possible estimates were given based on literature data.



## **6** CONCLUSION

Even though emission monitoring is a mature field with respect to research, the monitoring of emissions from a  $CO_2$ -capture plant requires considerable attention because of the type and number of possible components.

#### **Status of manual sampling:**

- 1) The range of physical properties of the components (boiling points, water solubility, acidity and thermal stability) requires numerous parallel sampling procedures.
- 2) Existing standardized gas sampling methods for amines, amides, alkylamines, and nitrosoamines are almost exclusively developed for work-place air measurements or ambient air measurements
- 3) No standards have been found for sampling and measurements of the mentioned components in a wet flue gas exiting from absorbers for amine based carbon capture. However,
  - a. Amines, ammonia, alkylamines and other basic compound can be sampled from flue gas by impingers with aqueous solution of sulfuric acid as absorbent
  - b. Aldehydes can be sampled from flue gas by impingers with aqueous solution containing 2.4-di-nitro-phenylhydrazine (DNPH) as derivatization agent
  - c. Amines can be sampled in a solution of 1-Naphthylisothiocyanate , though this method is only applicable for dry flue gases
- 4) There is no standardized methodology for sampling of amides and nitrosamines on solid absorbents that can handle the large amount of water that will be typical for flue gas from amine based carbon capture.
- 5) There is currently <u>no common</u> sampling method or strategy that can be applied simultaneously to a broad spectrum of different compounds/classes of compounds.
- 6) Expected thermal instability of components and side reaction limit the application of heated sampling systems

Further, the limited knowledge of type and amount of components emitted, their possible interference during sampling, handling and storage give rise to numerous open questions.

#### Manual sampling adapted to amine based CO<sub>2</sub>-capture plants

Considering the issues presented, a modified sampling system is suggested which resolves most probably most of the challenges today's sampling methods have.

- 1) Isokinetical sampling is performed with a cooled sample probe, the sample stream is directly transferred to a knock-out condenser (exit temperature 4°C) or a refrigerated cooler (subzero temperature)
- 2) The collected condensate can directly be transferred to analysis (see Subtask 4 for details /3/)
- 3) The dried sample gas stream can be subjected to several adsorption (solid) or absorption (liquid) units in parallel for specific sampling. Analysis of liquids can be performed analogous to point 2. Sampling on solid adsorbents is performed in line with recommendations for ambient air analysis without corruption of results through excess humidity.
- 4) Comprehensive analysis through combination of both analytical results (condensate and gas phase) is possible. With increased experience only one phase needs analysis.

The proposed sampling method is based on similar sampling for PCDD/PCDF; the applicability with respect to the component groups to be analysed here needs verification.

#### Storage of samples

Because of limited knowledge with respect to side reactions during storage, it is proposed to store samples in closed containers in a freezer.



#### Limit of detections

Even though the current report present limit of detections, these for ambient air measurements are "out-of-date". Methods are generally old and the development of analysis instruments with respect to low limit of detections and speciation are not incorporated. For a more thorough discussion we refer to Subtask 4 /3/.

#### High volume sampling

Accumulation of large amounts of liquid phase from the flue gas by isokinetically sampling and cooling of the gas stream to condense components with the apparatus presented in Figure 4-3 is straight forward. However, verification is necessary with respect to condensation temperature to ensure an appropriate sample composition for toxicological evaluations.



## 7 RECOMMANDATION AND FUTURE WORK

The number of possible components in the flue gas, with widely varying physical properties, possible thermal instability and unwanted side reactions (generation of artefacts), sum up the problem of manual sampling on a CO<sub>2</sub>-capture plant. No single standardized sampling method exists for the broad spectrum of compounds. As a consequence of this, the present status is that complex batteries of sampling principles and equipment need to be utilized in parallel or series to collect all groups of components. This complexity gives both technical and practical challenges.

#### Manual sampling at amine based CO<sub>2</sub>-capture plants

The evaluation of sampling methods is strongly recommended to build a knowledge base regarding emissions and sampling procedures for emission monitoring. Development of procedures needs attention; however, some of the work environment procedures can be adapted provided a suitable sample apparatus is available. Methods developed for ambient air (work environment) are strongly influenced by humidity and limited with respect to temperature. If humidity is above the dew point or temperature is considerably above room temperature, these methods can not be applied.

#### **Optimized manual sampling adapted to amine based CO<sub>2</sub>-capture plants**

Sampling procedures where the flue gas stream is dried in a knock-out condenser and/or subsequent refrigerated cold trap has potential as shown by the performed proof-of-concept at SINTEF. Versatility of the system combined with high resolution analysis of the condensate phase by e.g. mass spectroscopy based instruments needs further verification. Application of solid adsorbents to the dried gas streams is straight forward. Research and development is necessary to implement such a solution.

#### Future work:

Testing of the apparatus consisting of a knock-out condenser and/or knock-out condenser/refrigerated cold trap combination, with respect to efficient transfer of components from the flue gas to condensate phase is advised. The work should be performed in two stages, a bench scale (proof-of-concept) and pilot plant scale where the VOCC-test facility can be used to simulate wet flue gas from an absorber with possibility to include numerous absorbents or degradation products.

The following work is suggested:

- Testing of the efficiency of the proposed **knock-out condenser** to remove main obstacle: high flue gas humidity. Efficiency in terms of how much organic components are removed from the flue gas stream at a given dry gas exit temperature (e.g.: -10, 0, 4 and 20°C) and evaluated the reputability of procedure.
- Separate analysis of the condensate phase and solid adsorbent units to establish understanding of the split between phases
- Evaluation if sufficient analysis is possible when only the liquid phase is analyzed. It is expected that most of high boiling components will condense and therefore limited amount will be in the gas phase.

Practical implementation of the suggested work:

• Bench scale experiments where a complete control of the mass balance in a closed system is possible. The proposed bench scale apparatus consists of flue gas generation, knock-out condenser and absorption unit. Liquid samples and samples from the absorption unit are analysed. The closed system allows for assessment of the efficiency of the proposed sampling methodology.



- Bench scale experiments will also allow flue gases which contain components like nitrosamines and nitramines, provided a thermal catalytic system is installed in the off-gas pipe from the experiment to ensure destruction of harmful components.
- After evaluation of the initial proof-of-concept experiments with respect to applicability and efficiency of the system; the apparatus can be scaled up to be tested at the SINTEF VOCC test facility. Here verification of the entire system on a more realistic flue gas can be performed. Further importance of iso-kinetically sampling can be verified through variation of operation parameters on the test facility.



# **APPENDIX 1**

## Table A1-1: Properties of components (given from company)

	Component Name	Abbrev- iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable/ Decomp C <sup>o</sup>	LogP	pkA	Vapor pressure bar
	N-		62-75-9							EtOH,				
	Nitrosodimethylamine	NDMA		-28	152	1	284	284	284	Ether		-0,496	-3,63	6,08E-03
nes	N- Nitrosodiethylamin	NDEA	55-18-5	<25	175	1	62	62	62	EtOH, Ether		0,523	-3,14	2,21E-03
imi	N-Nitrosomorpholine	NMOR	59-89-2	29	140	s	130	130	130			-0,594	-5,72	1,67E-04
0S2	N-Nitrosopiperidin	NPIP	100-75-4	170?	229		27	27	27			0,438	-3,18	1,37E-04
V-Nita	N- Nitrosodiethanolamin	NDELA	1116-54-7	5	125	1	1000	1000	1000	EtOH, Ether	200	-1,37	-5,78	4,61E-10
4	N-Nitrosopiperazine		5632-47-3	Ş	264	1	1000	1000	303			-0.081	8.07	1.29E-05
	1,4-Di- Nitrospiperazine		140-79-4		406		148	148	148			-0.946	-4.82	2.61E-09
s	Methylamine		74-89-5	-94	-6	σ	1000	1000	1000			-0.472	10.66	5.29E
vlamine	Ethylamine		75-04-7	-81	16.6	<u>8</u>	1000	1000	1000			0.037	10,00	1,51E
	Dimethylamine		124-40-3	-93	7	<u></u> б	1000	1000	1000			-0.362	10,01	2.03E
Alk	Diethylamine		109-89-7	-50	55	1	1000	1000	1000			-0.657	10,76	2.91E-01
	Mono-ethanol-amine	MEA	141-43-5	10	171	1	1000	1000	1000	MeOH		-1 48	9.6	6.11E-04
	Di-ethanol-amine	DEA	111-42-2	28	268	s	1000	1000	1000	incon		-1.761	8.71	1.87E-06
ş	Piperazine		110-85-0	106	146	s	1000	1000	1000	Glycerol, EtOH		-1,5	9,55	5,40E-03
mine	1,2-Di-amino-ethane		107-15-3	8,5	116	1	1000	1000	1000	EtOH/Ben zene		-2,057	9,89	2,11E-02
Α	2-Amino-2-methyl-1- propanol	AMP	124-68-5	30	165	S	1000	1000	1000	Alcohols		-0,716	12,91	7,55E-04
	N-Methyl-di-ethanol- amine	MDEA	105-59-9	-21	247	1	1000	1000	1000	benzene alcohols		-0,619	14,41	5,75E-06
ides	Formamide		75-12-7	2,5	210	1	901	898	898	acetone	115°C /24/ 180°C	-1,51	16,5	2,56E-04
Am	Acetamide		60-35-5	81	222	s	123	123	123	alcohol, pyridine		-0,806	16,6	1,45E-04
hydes	Formaldehyde		50-00-0	-92	-19,5	g	198	198	198	alcohol,ethe r, benz.		0,35	-	4,61
Alde	Acetaldehyde		75-07-0	-121	21	g	53.7	53.7	53.7	alcohol, ether, benz.		-0,105	-	1,29



	Component Name	Abbrev- iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable/ Decomp C°	LogP	pkA	Vapor pressure bar
nts	Nitrogen	$N_2$	7727-37-9	-210	-192,8	g								
one	Water	H <sub>2</sub> O	773-18-5	0	100	1								
duu	Carbon Monoxide	CO <sub>2</sub>	630-08-0	-199	-191,5	g								
ts cc	Ammonia	NH <sub>3</sub>	7664- 41-7	-77	-33,5	g		31%						10.03
ie gi	Nitros Oxide	NO <sub>x</sub>	10024-97-2	-163	-151,8	g								
Flu	Sulphur Di-oxide	SO <sub>2</sub>	7446-09-5	-72	-10	g								



## Table A1-2: Properties of components, degradation products of piperazine from TQP4

Component Name	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	LogP	pkA	Vapor pressure bar
Ethanolnitramine	74386-82-6	nd	266		169	896	100		-0.806	6.34	1.63E-06
Dimethylnitramine	4164-28-7	58	187	s	176	176	176		-0.447	-7.1	1.18E-03
Methylnitramine	598-57-2	38	115	s	431	1000	1000		-0.598	6.51	2.60E-02
Methylamine	74-89-5	-94	-6	g	1000	1000	1000		-0.472	10.7	5.29E+00
Diethylamine	109-89-7	-50	55	1	1000	1000	1000		-0.657	10.8	2.91E-01
2-oxopiperazine	5625-67-2	116	307	s	1000	1000	611		-1.393	15.5	9.84E-07
2,5-piperazinedione / Glycine anhydride	106-57-0	111	574	s	286	286	286		-2.69	12.9	4.85E-16
Ethylendiamine	107-15-3	8.5	117	1	1000	1000	1000		-2.057	9.89	2.11E-02
1-PiperazinecaroxaldehydeN- Formylpiperazine	7755-92-2	205	292	s	1000	387	50		-0.539	8.58	2.56E-06
1-Acetylpiperazine	13889-98-0	218	258	s	1000	1000	1000		-1.433	8.5	1.89E-05
1,1'carbonylbis piperazine / 1,2- carbonylbis PZ urea	17159-16-9	nd	333.7		999	999	15		-0.11	9.06	1.79E-07
1-Piperazineethanol/ Hydroxyethylpiperaine	103-76-4	147	245	s	1000	1000	1000		-1.284	15	6.56E-06
N-(hydroxymethyl)-piperazine	90324-69-9	nd	213		1000	1000	209		-0.637	14.6	5.01E-05
N-Glycylglycine	556-50-3	210	453		1000	139	1000		-2.291	7.82	2.39E-12
Formic acid / formate	64-18-6	8.4	100.6	1	705	1000	1000		-0.54	3.74	4.87E-02
Acetic acid / acetate	64-19-7	16.6	117.1	1	197	1000	1000		-0.322	4.79	1.85E-02
Oxalic acid	144-62-7	189	365	S	1000	1000	1000		-1.077	1.38	3.35E-09
1-nitrosopiperazine	5632-47-3	nd	264.5		1000	1000	303		-0.081	8.07	1.29E-05
1,4-di-nitrosopiperazine	4164-37-8	195	492	S	1.5	1.5	1.5		-1.561	-8.8	3.16E-12
1-nitrosopiperazine	42499-41-2	127	307.8	s	1000	236	50		-0.917	7.58	8.91E-07
1,4-di-nitropiperazine	4164-37-8	195	492	s	1.5	1.5	1.5		-1.561	-8.8	3.16E-12
N-nitrosodi-methylamine	62-75-9	-28	152	1	284	284	284	EtOH, Ether	-0.496	-3.63	6.08E-03
Methylnitramine	598-57-2	38	115	s	431	1000	1000		-0.598	6.51	2.60E-02
Dimethylnitramine	4164-28-7	58	187	S	176	176	176		-0.447	-7.12	1.18E-03



## Table A1-3: Properties of components, degradation products MEA from TQP4

Component Name	Abbrev -iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable / Decomp C°	LogP	pkA	Vapor pressure bar
Mono-ethanol-amine		141-43-5	10	171	1	1000	1000	1000			-1.48	9.6	6.11E-04
Formic acid / formate		64-18-6	8.4	100.6	1	705	1000	1000			-0.54	3.74	4.87E-02
Acetic acid / acetate		64-19-7	16.6	117.1	1	197	1000	1000			-0.322	4.79	1.85E-02
Oxalic acid		144-62-7	189	365	s	1000	1000	1000			-1.077	1.38	3.35E-09
Propanoic acid/Propinoic acid		79-09-4	-21.5	141	1	95.6	1000	1000			0.188	4.79	5.64E-03
Hydroxy-acetic acid/glycolate/ glycolic acid		79-14-1	78	265	s	1000	1000	1000			-1.204	3.74	1.67E-06
Lactic acid/Lactate		50-21-5	16.8	227.6	1	804	1000	1000			-0.85	3.91	2.00E-05
Butanoic acid/Butyric acid/butyrate		107-92-6	-7.9	164	1	45	1000	1000			0.697	4.76	1.80E-03
Oxazolidin-2-one		497-25-6	89	324	s	453	453	453			-1.876	12.78	3.39E-07
1-(2_hydroxyethyl)-2- imidazolidinone,	HEIA/ HEI	3699-54-5	50	400	s	60	60	60			-0.919	4.57	6.09E-11
N-(2-hydroxyethyl)- ethylenediamine,	HEED /HEE /DA	111-41-1	-38	239	1	1000	1000	1000			-1.746	9.61	9.43E-06
N-(2-hydroxyethyl)- acetamide/N- acetylethanolamine/	HEA	142-26-7	63	291	S	1000	1000	1000			-1.336	14.56	2.80E-07
N-(2-hydroxyethyl)- Formamide/N- formylethanolamine/	HEF	693-06-1	nd	349		427	427	427			-2.706	14.31	3.77E-09
1-(2-hydroxyethyl)-2,5- Pyrrolidinone/N-(2- Hydroxyethyl)succinimide		18190-44-8	58	352	s	140	140	140			-1.406	14.2	3.15E-09
N-(2-Hydroxyethyl)- lactamide		5422-34-4	nd	380		718	716	718			-1.268	13.34	3.20E-09



Component Name	Abbrev -iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable / Decomp	LogP	pkA	Vapor pressure bar
										Co			
N,N-di(2-hydroxyethyl)- urea /MEA-urea		15438-70-7	83	445	s	1.5	1.5	1.5			-2.21	13.09	1.14E-12
N-(2-hydroxyethyl)-3-[(2- hydroxyethyl)amino]- Propanamide/ 3-hydroxy ethylamino-N-hydroxy		587876-41-											
ethyl propanamide N-(2-hydroxyethyl)-2- [(hydroxyethyl)amino]- acetamide/ 2-hydroxyethylamino-N- hydroxyethyl acetamide		3 144236-39- 5	nd	463		5.67	642	5.67			-2.499 -2.365	14.47	2.13E-13 2.52E-13
1-(2-hydroxyethyl)-2- piperazinone		59702-23-7	nd	340		1000	1000	1000			-1.238	7.68	1.19E-08
4-(2-hydroxyethyl)-2- piperazinone		23936-04-1	59	450	S	1000	1000	1000			-1.325	7.38	5.01E-09
2-((2-[(2- hydroxyethyl)amino]ethyl) amino)ethanol		4439-20-7	98	305	s	1000	1000	1000			-2.017	9.42	1.06E-07
2-methylaminoethanol		109-83-1	-4.5	155	1	1000	1000	1000			-1.062	14.84	1.47E-03
2,2'-[[2-[(2- hydroxyethyl)amino]ethyl] imino]bis-Etha nol	THEE D	60487-26-5	nd	375		1000	1000	1000			-1.518	14.39	4.89E-10
1,3-bis(2-hydroxyethyl)-2- Imidazolidinone/BHEI		71298-49-2	nd	385		89	89	89			-1.28	14.62	2.03E-10
Acetone		67-64-1	-94	55	1	94.7	94.7	94.7			-0.42	-	4.64E-01
Nitric acid/Nitrate		7697-37-2	-41	83.2	1	878	878	878			-0.77	-	6.64E-02
Nitrous acid/Nitrite		7782-77-6	-	-		474	1000	1000			-0.317	3.15	
Oxalamide/oxamide		471-46-5	-	262		320	320	320		350	-1.465	13.28	1.43E-05
1-(2-Hydroxyethyl)- imidazole	HEI	1615-14-1	36	316	s	1000	1000	696			-0.449	13.8	2.29E-07
2,6-dimethyl-4- pyridinamine		3512-80-9	186	246	S	1000	1000	48					



Component Name	Abbrev -iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable / Decomp	LogP	pkA	Vapor pressure bar
					-					C°			
1H-imidazole-2- carboxaldehyde/2-			105	201		105							
ımıdazolecarbox-aldehyde		10111-08-7	195	296		135	20	21			-0.082	11.48	1.91E-06
1-methyl-1H-imidazole-2- carboxaldehyde		13750-81-7	35	251	S	1000	19	19			0.33	4.17	2.83E-05
1-hydroxyethyl-3- homopiperazine		no cas	nd	nd	nd	nd	nd	nd			nd	nd	nd
N-ethyl-N'-(2- hydroxyethyl)- Urea/Hydroxyethylethyle													
neurea	HEEU	29346-51-8	nd	345		0.49	0.49	0.49			-0.925	14.43	5.73E-09
N,N-bis (hydroxyethyl)- piperazine	BHEP/ HEP	122-96-3	134	305	s	1000	1000	1000			-1.612	14.66	1.01E-07
Glycine		56-40-6	86	241	s	357	112	432		240	-0.928	2.46	1.64E-05
Hydroxy-Acetaldehyde		141-46-8	76	131	s	733	733	733			-1.604	13.34	5.53E-03
2-imidazolidinone		120-93-4	132	358	s	8	7.9	7.9			-1.242	14.58	3.33E-08
Morpholine		110-91-8	-5	128	1	1000	1000	689			-0.791	8.97	1.39E-02
N –nitroso- dimethylamine		62-75-9	-28	152	1	284	284	284	EtOH, Ether		-0.496	-3.63	6.08E-03
Nitroso-morpholine		59-89-2	29	140	s	130	130	130			-0.594	-5.72	1.67E-04
Methylnitramine		598-57-2	38	115	S	431	1000	1000			-0.598	6.51	2.60E-02
Dimethylnitramine		4164-28-7	58	187	s	176	176	176			-0.447	-7.12	1.18E-03
Ethanolnitramine		74386-82-6	nd	266		169	896	100			-0.806	6.34	1.63E-06
2-methyl-3-nitroso- oxazolidine		39884-53-2	nd	226		74	74	74			-0.178	-5.9	1.60E-04
N-nitroso ditethanolamine		1116-54-7	nd	125	1	1000	1000	1000	EtOH, Ether	200	-1.37	-5.78	4.61E-10



## Table A1-4: Properties of components, degradation products MDEA from TQP4

Component Name	Abbrev- iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable / Decomp C <sup>o</sup>	LogP	pkA	Vapor pressure bar
N-methyl ditabanalamina	MDEA	105 50 0	21	247	1	1000	1000	1000			0.610	14 41	5 75 06
4-methyl-1- Piperazineethanol/HE	MDEA	103-39-9	-21	247	1	1000	1000	1000			-0.019	14.41	5.75E-00
MP/HMP		5464-12-0	nd	234		999	999	999			-0.908	14.96	1.25E-05
1,4 dimethylpiperazine		106-58-1	nd	136.1		1000	1000	1000			-0.204	8	1.00E-02
Triethanolamine	TEA	102-71-6	21	335	1	1000	1000	864			-0.988	14.17	1.12E-08
Formic acid/formate		64-18-6	8.4	100.6	1	705	1000	1000			-0.54	3.74	4.87E-02
Acetic acid/acetate		64-19-7	16.6	117.1	1	197	1000	1000			-0.322	4.79	1.85E-02
Oxalic acid		144-62-7	189	365	s	1000	1000	1000			-1.077	1.38	3.35E-09
Methylamine		64-18-6	8.4	100.6	1	705	1000	1000			-0.54	3.74	4.87E-02
N-nitroso ditethanolamine		1116-54-7	nd	125	1	1000	1000	1000	EtOH, Ether	200	-1.37	-5.78	4.61E-10
2-(methylnitroso-amino) ethanol		26921-68-6	nd	277		988	988	988			-0.911	14.13	1.16E-06
Formaldehyde		50-00-0	-92	-21	g	198	198	198	alcohol,et her, benz.		0.35	-	4.61
Acetaldehvde		75-07-0	-121	21	g	53.7	53.7	53.7	alcohol,et her. benz.		-0.105	_	1.29
Formamide		75-12-7	2.5	210	1	901	898	898	acetone		-1.51	16.5	2.56E-04
Dimethylamine		124-40-3	-93	7	g	1000	1000	1000			-0.362	10.73	2.030
Ethylamine		75-04-7	-81	16.6	g	1000	1000	1000			0.037	10.64	1.51
Diethylamine		124-40-3	-93	7	g	1000	1000	1000			-0.362	10.73	2.03
N-nitroso- dimethylamine		62-75-9	-28	152	1	284	284	284	EtOH, Ether		-0.496	-3.63	6.08E-03
Methylnitramine		598-57-2	38	115	s	431	1000	1000			-0.598	6.51	2.60E-02
Dimethylnitramine		4164-28-7	58	187	s	176	176	176			-0.447	-7.12	1.18E-03
Nitroso-morpholine		59-89-2	29	140	s	130	130	130			-0.594	-5.72	1.67E-04



## Table A1-5: Properties of components, degradation products AMP from TQP4

Component Name	Abbrev- iation	CAS. Nr.	Melting point	Boiling point	Aggregate state at room temp.	Solubility in water g/L pH2	Solubility in water g/L pH7	Solubility in water g/L pH10	Other solvents	Thermally stable / Decomp C <sup>o</sup>	LogP	pkA	Vapor pressure bar
2-amino-2- methylpropanol (AMP)		124-68-5	23	167	s	1000	1000	1000			-0.716	12.91	7.55E-04
4,4-dimethyl-2- Oxazolidinone		26654-39-7	48	272	1	175	176	175			-0.96	12.91	8.23E-06
2-methyl-2- (methylamino)- 1- Propanol		27646-80-6	nd	162		1000	1000	1000			-0.297	15.9	1.01E-03
3,4,4-trimethyl oxazolidin-2-one		15833-17-7	nd	243		21	21	21			0.63	-1.21	4.31E-05
Formic acid/formate		64-18-6	8.4	100.6	1	705	1000	1000			-0.54	3.74	4.87E-02
Acetic acid/acetate		64-19-7	16.6	117.1	1	197	1000	1000			-0.322	4.79	1.85E-02
Oxalic acid		144-62-7	189	365	s	1000	1000	1000			-1.077	1.38	3.35E-09
4,4 dimethyl-2- isopropyl-3- nitrosooxazolidine*		39884-58-7	nd	253		6.5	6.5	6.5			1.601	-5.9	3.95E-05
Nitro 2-amino-2- methylpropanol		no cas	nd	nd		nd	nd	nd			nd	nd	
Methylamine		74-89-5	-94	-6	g	1000	1000	1000			-0.472	10.66	5.29
Ethylamine		75-04-7	-81	16.6	g	1000	1000	1000			0.037	10.64	1.51
Dimethylamine		124-40-3	-93	7	g	1000	1000	1000			-0.362	10.73	2.03
Diethylamine		109-89-7	-50	57.3	1	1000	1000	1000			-0.657	10.76	2.91E-01
Formaldehyde		50-00-0	-92	-21	g	198	198	198	alcohol,et her, benz.		0.35	-	4.61
Acetaldehyde		75-07-0	-121	21	g	53.7	53.7	53.7	alcohol,et her, benz.		-0.105	-	1.29
Formamide		75-12-7	2.5	210	1	901	898	898	acetone		-1.51	16.5	2.56E-04
N-nitroso- dimethylamine		62-75-9	-28	152	1	284	284	284	EtOH, Ether		-0.496	-3.63	6.08E-03
Methylnitramine		598-57-2	38	115	s	431	1000	1000			-0.598	6.51	2.60E-02
Dimethylnitramine		4164-28-7	58	187	s	176	176	176			-0.447	-7.12	1.18E-03



## **APPENDIX 2**

## Table A2-1: Overview Guideline and Standards relevant for sampling of flue components / analysis thereof

Comp- onent	Identifier	Title / Method	Sample gas preparation / Absorbent/Adsorbent phase and type	Analytical method (examples)	Estimated limit of detection for original procedure (where available)
0	VDI 2459, Sheet 1; 2000	Gaseous emission measurement - Determination of carbon monoxide concentration using flame ionisation detection after reduction to methane	Particle removal by filter and gas drying with gas cooler (2°C)	Online: FID	
	EN 15058	Stationary source emissions - Determination of the mass concentration of carbon monoxide (CO) - Reference method: Non-dispersive infrared spectrometry	Particle removal by filter and gas drying	Online: NDIR	
CO <sub>2</sub>	ISO 12039	Stationary source emissions Determination of carbon monoxide, carbon dioxide and oxygen Performance characteristics and calibration of automated measuring systems		Online: IR- detector	Uncertainty (sum sampling + analysis +/- 8%
O <sub>2</sub>	EN 14789	Stationary source emissions - Determination of volume concentration of oxygen (O <sub>2</sub> ) - Reference method – Paramagnetism		Online: Zirconium Oxide Paramagnetic	
	EN 15058	Stationary source emissions - Determination of the mass concentration of carbon monoxide (CO) - Reference method: Non-dispersive infrared spectrometry		Online: NDIR	
H <sub>2</sub> O	VDI 2066 Sheet 1: 2006	Particulate matter measurement - Dust measurement in flowing gases - Gravimetric determination of dust load	Collection of condensate and adsorption on silica gel.	Gravimetric method	Limit of detection: 0,5 vol% Uncertainty (sum sampling + analysis +/- 10%
	EN 14790	Stationary source emissions. Determination of water in ducts (reference method)		Gravimetric method	
NO <sub>x</sub> (NO and	VDI 2456	Stationary source emissions - Reference method for determination of the sum of nitrogen monoxide and nitrogen dioxide - Ion chromatography method	Particle removal by filter and gas drying with gas cooler (2°C)	Ion Chromatography	
NO <sub>2</sub> )	EN 14792	Stationary source emissions. Determination of mass concentration of nitrogen oxides (NOx). Reference method: Chemiluminiscence	Particle removal by filter and gas drying with gas cooler (4°C)	Chemiluminisce nce	
NH3	VDI 2461 Sheet 2: 1976 (withdrawn)	Gaseous air pollution measurement; Measurement of ammonia gas concentration; NESSLER's solution method	Particle removal and absorption in H <sub>2</sub> SO <sub>4</sub> by means of two wash bottles in series (three bottles for high water load; first empty)	Ion Chromatography	LOD 20µg/sample Standard deviation <2µg



Comp- onent	Identifier	Title / Method	Sample gas preparation / Absorbent/Adsorbent phase and type	Analytical method (examples)	Estimated limit of detection for original procedure (where available)
	Värmeforsks mäthåndbok, ch. 5.14		Particle removal and absorption in H <sub>2</sub> SO <sub>4</sub> by means of two wash bottles in series (three bottles for high water load; first empty)	Photometric method	Limit of detection: 0,004 mg/Nm <sup>3</sup> Sampling gas volume: 0,8 Nm <sup>3</sup> dry gas Uncertainty (sum sampling + analysis +/- 12%
PCDD/ PCDF & PCB	DIN EN 1948-1; 2006 EN 1948-2: 2006	Emissions from stationary sources – Determination of the mass concentrations of PCDD/PCDF and dioxine like PCBs – Part 1: Sampling Emissions from stationary sources – Determination of the mass concentrations of PCDD/PCDF and dioxine like PCBs – Part 2: Extraction and cleanup	Iso-kinetically extraction with cooled probe Collection of condensate, particle filter and adsorbtion of gaseous components on XAD-2 resin	Gas chromatograph with dual column system and high	Sample volume 10 m <sup>3</sup> Limit of detection 1 – 5 pg for each congener Uncertainty (sum sampling + analysis +/-
	EN 1948-3: 2006	Emissions from stationary sources – Determination of the mass concentrations of PCDD/PCDF and dioxine like PCBs – Part 3: Identification and quantification	Extraction of all three phases to determine total concentration	resolution mass spectrometer	31-36%
РАН	ISO 11338-1; 2003 ISO 11338-2; 2003	Stationary source emissions – Determination of gas and particle-phase polycyclic aromatic hydrocarbons – Part 1: Sampling Stationary source emissions – Determination of gas and particle-phase polycyclic aromatic hydrocarbons – Part 2: Sample preparation, clean-up and determination	See PCDD/PCDF	High Performance Liquid Chromatography	Sample volume 10 m <sup>3</sup> Limit of detection 10 – 15 pg for individual component Uncertainty (sum sampling + analysis +/- 16 - 26%
ТОС	EN 12619; 1999	Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon at low concentrations in flue gases - Continuous flame ionisation detector method		Online: Flame	
	EN 13526; 2002	Stationary source emissions - Determination of the mass concentration of total gaseous organic carbon in flue gases from solvent using processes - Continuous flame ionisation detector method		Detector	
VOC	EN 13649; 2002	Stationary source emissions – Determination of the mass concentration of individual gaseous organic compounds – Activated carbon and solvent desorption method	Adsorption on activated carbon and subsequent solvent extraction	Solvent desorption and gas chromatography	
	VDI 3862-1; 1990	Gaseous emission measurement; measurement of aliphatic aldehydes (C1 to C3) MBTH (3-methyl-2-benzothiazolinone hydrazone) method	Liquid absorbent: MBTH, applicable for formaldehydes		
Aldehyde s	VDI 3862-2; 2000	Determination of gaseous emissions – Measurement of aliphatic and aromatic aldehydes and ketones using the DNPH-procedure – Impinger method	Liquid absorbent: DNPH	HPLC	
	VDI 3862-3;	Gaseous emission measurement - Measurement of aliphatic and aromatic	Solid absorbent: DNPH	HPLC	



Comp- onent	Identifier	Title / Method	Sample gas preparation / Absorbent/Adsorbent phase and type	Analytical method (examples)	Estimated limit of detection for original procedure (where available)
	2000	aldehydes and ketones by DNPH method - Cartridges method	impegnated Activated carbon		,
	VDI 3862-4; 2001	Gaseous emission measurement - Mesurement of formaldehyde by the AHMT method (alkaline method)	Liquid absorbent: alkaline solution AHMT		
	VDI 3862-5; 2008	Gaseous emission measurement - Measurement of lower aldehydes especially acrolein with the 2-HMP-method - GC-method	Liquid absorbent 2-HMP on fixed sorption material Desorption toluene	GC	
	VDI 3862-6; 2004	Gaseous emission measurement - Measurement of formaldehyde by the acetylacetone method	Liquid absorbent: acetylacetone	photometric or fluorometric analyses	
	VDI 3862-7; 2004	Gaseous emission measurement - Measurement of aliphatic and aromatic aldehydes and ketones by the DNPH method - Impinger/carbon tetrachloride method	Liquid absorbent DNPH combined with CCl <sub>4</sub> Derivatization to Hydrozones		
	Method 430; 1991	California Environmental Protection Agency, Determination of Formaldehyde and Acetaldehyde in Emissions from Stationary Sources, Method 430 (not validated for high humidity applications)	Impinger, Absorbent DNPH	HP-LC & UV;	0,1 μg/l
	VDI 2547, part 1 1997	Gaseous emission measurement - Chromatographic determination of organic compounds - Fundamentals		Gas Chromatograph	
	VDI 2457 part 2: 1997	Gaseous emission measurement - Gas chromatographic determination of organic compounds - Sampling by absorption in a solvent (2-(2- methoxyethoxy)ethanol, methyldiglycol) at low temperature	Adsorption on solids inpregnated with (2-(2-methoxyethoxy)ethanol, methyldiglycol)	Gas Chromatograph	
Amines	VDI 2457 part 3: 1996	Gaseous emission measurements - Gas chromatographic determination of organic compounds - Determination of substituted anilines - Sampling by solid phase adsorption	Adsorption on solids		
	VDI 2457 part 4: 2000	Gaseous emission measurement - Chromatographic determination of organic compounds - Sampling of acidic components in alkaline aqueous solution; Analysis by ion chromatography	Absorption in alkaline solution	Ion Chromatography	
	VDI 2457 part 5: 2000	Gaseous emission measurement - Chromatographic determination of organic compounds - Sampling in gas vessels, gas chromatographic analysis	Collection in gas vessel	Gas Chromatograph	
	VDI 3481 Part 2; 1998	Gaseous emission measurement - Determination of gaseous organic carbon in waste gases - Adsorption on silica gel	Adsorption on Silica Gel		
	VDI 3481 Part 3; 1995	Gaseous emission measurement - Determination of volatile organic compounds, especially solvents, flame ionization detector (FID)		Online FID	



	Component Name	Abbrev- iation	CAS. Nr.	Sampling procedure	Absorbent / Adsorbent	Analytical method	Estimated limit of detection for original procedure (where available)	Comment regarding applicability
	Volatile Nitrosoamine Mixture I	NDMA NDEA NDPA NDBA NPIP NPYR NMOR		OSHA 27	Thermosorb-N/ Ascorbic acid- impregnated glass fibre filters	desorbed with a 75/25 (v/v) dichloromethane/methanol solution; gas chromatography with Thermal Energy Analyzer detection	75 L at 1 l/min Sampling rate 0.2 – 2 l/min	
	Volatile Nitrosoamine Mixture II	NMEA NDiPA NMBA NEBA NPBA NDAmA		OSHA 38	Thermosorb-N/ Ascorbic acid- impregnated glass fibre filters	desorbed with a 75/25 (v/v) dichloromethane/methanol solution; gas chromatography with Thermal Energy Analyzer detection	75 L at 1 l/min; Sampling rate 0.2 – 2 l/min	
	Volatile Nitrosoamine			Milia-Kemi	Thermosorb-N	GC-MS / GC-NP		
	Semi-volatile or solid Nitrosamines			Prøvetagningsmanual. Method Nr. G14 /25/	Impregnated Filters combined with soli absorbent (Thermosorb N)			
	N- Nitrosodimethylamine	NDMA	62-75-9	Miljø-Kemi Prøvetagningsmanual method Nr: G-14	Thermosorb N	GC-MS / GS-NP		
				OSHA 6	Two Florisil adsorbent tubes in series, pretreated with 10 mg of DL-α- tocopherol,	desorption with a solution of equal methylene chloride and methyl alcohol Analysis GC & Chemiluminescene	25 L at 0.2 L/min LOD: 6.4 μg/m <sup>3</sup>	
samines	N- Nitrosodiethylamin	NDEA	55-18-5	Miljø-Kemi Prøvetagningsmanual method Nr: G-14	Thermosorb N	GC-MS / GS-NP		
N-Nitro				OSHA 13	Two Florisil adsorbent tubes in series, pretreated with 11 mg of DL-α-	desorption with a solution of equal methylene chloride and methyl alcohol	25 L at 0.2 L/min LOD: 0.4 μg/m <sup>3</sup>	

## Table A2-2: Sampling Methods for individual components / component groups from ambient air analysis



	Component Name	Abbrev- iation	CAS. Nr.	Sampling procedure	Absorbent / Adsorbent	Analytical method	Estimated limit of detection for original procedure (where available)	Comment regarding applicability
					tocopherol,	Analysis GC & Chemiluminescene		
	N-Nitrosomorpholine	NMOR	59-89-2	Miljø-Kemi Prøvetagningsmanual method Nr: G-14	Thermosorb N	GC-MS / GS-NP		
				OSHA 17	Two sampling tubes in series, Polar Partition and the second tube contains Florisil; both adsorbents are coated with ascorbic acid		40 L at 0.2 L/min LOD: 0.4 μg/m <sup>3</sup>	
	N-Nitrosopiperidin	NPIP	100-75-4	Miljø-Kemi Prøvetagningsmanual method Nr: G-14	Thermosorb N	GC-MS / GS-NP		
	N- Nitrosodiethanolamin	NDELA	1116-54- 7	OSHA 31	Gelman Type A glass fiber filters; extracted with 2-propanol	gas chromatography (GC) with Thermal Energy Analyzer (TEA)	480 L @ 2 L/min Quantification limit: 0.42 μg/m <sup>3</sup>	
	N-Nitrosopiperazine		5632-47- 3					
	1,4-Di- Nitrospiperazine		140-79-4					
	Alkylamines			OSHA	Absorption in 1- napthylisothiocyanate	HPLC		
	Methylamine		74-89-5	OSHA 40		desorbed with 5% (w/v)	10 L @ 0.2 L/min Quantification limit: 35 μg/m <sup>3</sup>	
	Ethylamine		75-04-7	OSHA 36; 1982	sampling tubes containing	NBD chloride in tetrahydrofuran (with a small amount of sodium bicarbonate present), heated	Sampling rate 101@ 0.2l/min LOD 29 µg/m HPLC-UV	
les	Dimethylamine		124-40-3	OSHA 34; 1982	10% NBD chloride by weight	in a hot water bath, and analyzed by high- performance liquid chromatography using a	Sampling rate 101@ 0.2l/min LOD: 43 µg/m <sup>3</sup> HPLC-UV	
Alkylamin	Diethylamine		109-89-7	OSHA 41; 1982		fluorescence or visible detector.	Sampling rate 101@ 0.2l/min LOD 160 µg/m <sup>3</sup> HPLC-UV	



	Component Name	Abbrev- iation	CAS. Nr.	Sampling procedure	Absorbent / Adsorbent	Analytical method	Estimated limit of detection for original procedure (where available)	Comment regarding applicability
				NIOSH 3509; 1994	Glass Midget Impinger (SKC 225-36-1)	IC		
	(Mono-) Ethanol-amine	MEA	141-43-5	OSHA PV2111	XAD-2; coated with NIT	HPLC-UV	Sampling rate 101@0.1 l/min Target concentration 6 mg/m3	Partially validated
	Di-ethanol-amine	DEA	111-42-2	OSHA PV2018, 1987 (only partly evaluated)	XAD-2 (SKC 226-30-18)	GC-MS / GS-NP HPLC-UV	Sampling rate 101@0.1 l/min Target concentration 15 mg/m3	
	Piperazine dihydrachlorine		110-85-0	OSHA CSI*	37mm glass fiber filter (SKC 225-709)	GC-NPD		
	1,2-Di-amino-ethane		107-15-3	NIOSH 2540	XAD-2 (SKC 226-30-18)	HPLC-UV		
	2-Amino-2-methyl-1- propanol	AMP	124-68-5	OSHA PV2145	XAD-2 / Glass Fiber Filter (SKC 226-30-16)	HPLC-UV		
	N-Methyl-di-ethanol- amine	MDEA	105-59-9					
	Acetamides /26/			DS/EN 689	Glass fibre/ quartz wool filters and Water absorber			
des	Formamide		75-12-7	OSHA CSI /27/	Silica gel (SKC 226-10)	GC-NDP		
Ami	Acetamide		60-35-5	OSHA PV2084; 1987 (only partly evaluated)	Silica gel (SKC 226-10)	GC-NDP		
	Aldehydes/ ketones			VDI 3862-2	Glass fibre/ quartz wool filters; DNPH-conversion to hydrazones			
	Aldehydes Screening Methods			NIOSH 2539; 1994	XAD-2 (SKC 226-118)	GC-FID & GC-MS		
nydes	Formaldehyde		50-00-0	NIOSH 2539	XAD-2 (SKC 226-118)	GC-FID & GC-MS		
Aldel	Acetaldehyde		75-07-0	NIOSH 2539	XAD-2 (SKC 226-118)	GC-FID & GC-MS		



### REFERENCES

1 Wittgens, B., A. Einbu, A. Brunsvik, K. Zahlsen, E. Hunnes, "Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO2 capture. Subtask 1: Design of Sampling Points in treated flue gas"; SINTEF Report F16137, 2010

2 Wittgens, B., A. Einbu, A. Brunsvik, K. Zahlsen, *Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO<sub>2</sub> capture. Subtask 3: Online Sampling", SINTEF Report F16785, 2010* 

3 Zahlsen, K. A. Brunsvik, B. Wittgens, A. Einbu, *"Establish sampling and analytical procedures for potentially harmful components post combustion amine based CO<sub>2</sub> capture. Subtask 4: Literature Study"*, SINTEF Report F16585, 2010

4 Wittgens, B.; H.K. Kvamsdal, O. Juliussen, H. Kolderup & A. Einbu; "CO2-Kårstø – Concept study no. 9, selection of gas analyser and monitoring system", SINTEF Report F6335, 2008

5 BREF: "General Principles of Monitoring" <u>http://eippcb.jrc.es/reference</u> 6 Environment agency: <u>http://www.environment-</u>

agency.gov.uk/buisiness/regulations/31849.aspx

7 EPA: Forum on Environmental Measurements: <u>http://www.epa.gov/fem/methcollectns.htm</u> 8 <u>http://en.wikipedia.org/wiki/Humidity</u>

9 Technical guidance Note 8 Monitoring) M9 - Ambient monitoring methods, Environment Agency, 2000; <u>http://www.environment-agency.gov.uk/business/regulation/31831.aspx</u>

10 Assessment of Monitoring Arrangements: Emissions to Air Version 3 January 2010; <u>http://www.environment-agency.gov.uk/business/regulation/31831.aspx</u>

11 Applications under the Environmental Permitting Regulations (EPR) Assessment of Monitoring Arrangements: Emissions to Air Version 3 January 2010; <u>http://www.environment-agency.gov.uk/business/regulation/31831.aspx</u>

12 Technical guidance Note (Monitoring) M2: Monitoring Stack Emission to air, Environment Agency, Version 7 August 2010; <u>http://www.environment-</u>

agency.gov.uk/business/regulation/31831.aspx

13 Personal communication: Eli Hunnes, Molab

14 Personal communication with Peter Zemek, MIDAC Cooperation

15 Fostås, B.F.; M. Sjøvoll, S. Pedersen, "Flue gas degradation of amines", Climit project 190651, 2010

16 ISO11338-2:2003

17 EN 1948-1 Emissions from stationary sources – Determination of the mass concentrations of PCDD/PCDF and dioxine like PCBs – Part 1: Sampling; 2006

18 Dräger Röhrchen & CMS Handbuch, Juli 2008;

http://www.draeger.com/media/10/01/87/10018753/roehrchen\_cms\_handbuch\_br\_9092084\_de.p df

19 NIOSH Manual of Analytical methods; <u>http://www.cdc.gov/niosh/docs/2003-154/</u>

20 OSHA Alphabetic Table of Methods; http://www.osha.gov/dts/sltc/methods/toc.html

21 EN 13284-1 Stationary source emissions. Determination of low range mass concentration of dust – Part 1: Manual gravimetric method; 2002

22 Andersson, K. C. Hallgren, J.O. Levin and C.A. Nilsson: Determination of Ethylendiamine in Air Using Reagent coated Adsorbent tubes and High Performance Liquid Chromatography on the 1-Naphthylisothiourea Derivate, American Industrial Hygiene Association Journal, 46 (4): 225-229, 1985

23Kolderup, H., E. da Silva, T. Mejdell, A. Tobiesen, G. Haugen, K. A. Hoff, K. Josefsen, T. Strøm (SINTEF); O. Furuseth, K. F. Hanssen, H.Wirsching, T. Myhrvold, K. Johnsen (DNV), *"Emission Reducing Technologies H&ETQP Amine6"*, SINTEF Report, 2010



24 Kakumoto, t., K. Saito and A Imamura, Thermal decomposition of Formamide: Shock Tube Experiments and ab Inito Calculations; J. Phys. Chem., 1985, 89, 2286-2291

25 Miljø-Kjemi's Prøvtagningsmanual for arbeidshygiejniske Luftforureningsmålinger, 2. utgave, Miljø-Kjemi Forlag.

26 EN 689: Workplace atmospheres. Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy, 1996

27 OSHA CSI: Evaluation Guideline for Air Sampling methods; Utilizing Chromatographic Analysis