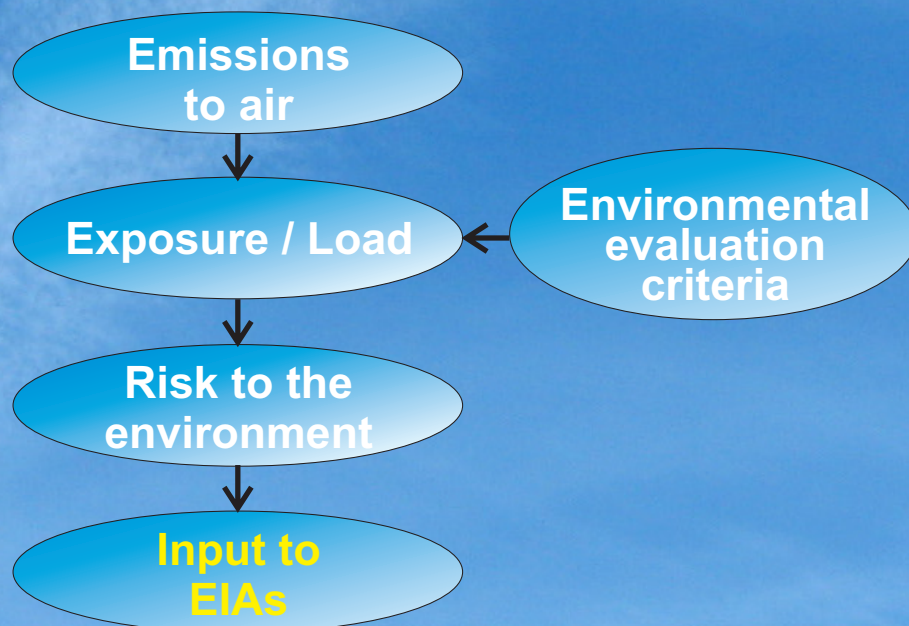# Task 4 Report:
Evaluation of Analytical Methods for Amine Related Emissions and Degradation Products in Emission and Ambient Air

Phase I: CO$_2$ and Amines Screening Study for Environmental Risks

Emissions to air

Exposure / Load

Environmental evaluation criteria

Risk to the environment

Input to EIAs

Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air

Phase I

Christian Dye, Norbert Schmidbauer, and Martin Schlabach

Preface

CO$_2$ capture and storage (CCS) has been proposed for two Norwegian gas-fired power plants as a measure to reduce CO$_2$ emissions to the atmosphere. A leading technology for CO$_2$ capture is through the use of amines. The *CO$_2$ and Amines Screening Study Project* began with *Phase I* in May 2008. The project was initiated by the Norwegian Institute for Air Research (NILU) based on the results of an expert meeting in October 2007, and discussions with the Norwegian Pollution Control Authority (SFT). The expert meeting and the following Phase I project is based upon the concern that the emissions from CO$_2$ capture using amines could be potentially harmful to the environment and human health, and that the existing information regarding these subjects were quite limited, thus demanding further examination and analysis.

The project was graciously sponsored by the following:

- Gassnova SF (CLIMIT)
- Statoil Hydro ASA
- Shell Technology Norway AS

The following institutes participated in the project:

- Centre for Theoretical and Computational Chemistry (CTCC) Department of Chemistry at the University of Oslo, responsible for the theoretical study on the atmospheric degradation of selected amines (Task 3).
- The Norwegian Institute of Public Health (FHI), responsible for the effects to human health (Task 7).
- Norwegian Institute for Nature Research (NINA), responsible for the effects to terrestrial ecosystems (Task 8).
- Norwegian Institute for Water Research (NIVA), responsible for the effects on freshwater ecosystems (Task 9).
- Norwegian Institute for Air Research (NILU), responsible for project management/coordination, including the chemical screening report, models report, worst case study report, and the summary report (Task 1, 2, 4, 5, 6, and 10).

The project sponsors comprised the Steering Committee, which gave useful guidance to the project and its administration. The project sponsors function within the Steering Committee also gave them an active role in reviewing all project reports and documentation.

Contents

Summary

This report describes the chemical analysis methods evaluated and partly tested for chemical screening of the CO_2 capture process. The methods are designed to cover a wide chemical range of compounds by using several specialized sampling and analysis techniques.

Experience from other technical processes using amines for CO_2 capture, literature surveys and theoretical evaluations revealed different chemical compounds as potential pollutants from the CO_2 capture process at natural gas power plants: amines, substituted amines, amides, N-nitramines and N-nitrosamines.

During this initial phase two complementary analytical methods have been evaluated: (1) exposure of adsorbent tubes followed by thermo desorption and analysis by gas chromatography and mass spectrometry (TD-GC/MS) and (2) exposure of impregnated filters followed by extraction and analysis by liquid chromatography and mass spectrometry on a time-of-flight instrument (IF + LC/MS). Due to lack of relevant stack samples the evaluation was based on laboratory experiments and former experience from real samples collected from vulcanisation industry (Swedala, Sweden 1997) and ambient air samples Dye 2006, Wiklund 2008. Both methods can give important information on the existence and concentration of compounds directly emitted or secondarily formed by the CO_2 capture process.

The three major advances of the TD-GC/MS method are (1) separation capacity, (2) library identification, and (3) quantification. Even without isolated standard compounds available, this method allows a semi-quantitative estimation of the concentrations of all identified compounds. With isolated standard compounds this method can become fully quantitative and fully validated. The major drawback of GC-methods is their weakness towards the separation of polar compounds. Since the principle of gas chromatography requires analytes in the gas phase, this method is in no case applicable for thermo-labile compounds.

LC/MS, on the other hand, has been shown to be very suitable for polar compounds, even for thermo-labile substances. The limiting prerequisites for LC/MS analysis are that the analytes are soluble, stable in solution and ionizable within the ion source of the LC/MS instrument. For LC/MS the use of libraries for identification is very limited. However, a time-of-flight type LC/MS can give the sum formula of the compound. The sum formula together with information obtained by induced fragmentation and retention time, is often enough to identify a compound. The most important drawback of LC/MS is that the response factor can vary several orders of magnitude from one compound to another. Furthermore, coeluting compounds may cause suppression of the analyte signal. This means that the method must be calibrated and validated with isolated standards for quantification.

In this initial study focus was on air samples and no other matrix type has been evaluated. With our experience from other method development projects we believe that it will be possible to adjust the TD-GC/MS method to both water and solid samples like soil or sediment. However, the LC/MS must be adapted and tested for each new type of matrix since interfering compounds can cause severe suppression problems.

Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air

Phase I

1 Introduction

Several methods exist for CO_2 capture, amine capture is just one of these. In the process that is described for CO_2 capture using amines, a series of possible degradation products with possible impact to the environment and human health may be formed. These substances may have a wide spectre of chemical characteristics, such as high pK_a, low pK_a, polar substituents, multifunctional and monofunctional groups.

As described in the proposal the goal of this task is **to establish a screening method for emissions to air** to identify the compounds in emissions and in the ambient air.

No real emission samples from amine-based CO_2-capture processes have been made available for training and testing. Furthermore, the composition of the intended amine-mixture is - at the present time - not given. In this situation, it was necessary to adjust the original plan and it was decided to focus on evaluation of analysis screening methods for amine related emissions and degradation products together with initial testing for selected amines.
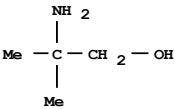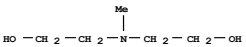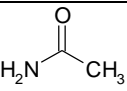
This report describes feasible chemical analysis methods for chemical screening of compounds emitted by amine based CO_2 capture. The methods are designed to cover a wide chemical range of compounds by using several specialized sampling and analysis techniques.

The outcome of Phase I will be used in Phase II, as the necessary chemicals or facilities are available, to verify and quality assure the analytical screening methods proposed in this report. Other aspects of Phase II will be the development of specialized methods dedicated to the exact quantification of compounds of particular interest and the development of analytical methods for other matrices of environmental concern like water or soil.

2 Compounds of interest

Both experience from other technical processes using amines for CO_2 capture, literature survey and theoretical evaluations performed in task 3 of this project (Bråten et al., 2008 and Knudsen et al., 2008) revealed different chemical compounds as potential degradation products from CO_2 capture process at natural gas power plants: amines, substituted amines, amides, N-nitramines and N-nitrosoamines. Of these, some typical example compounds are listed in Table 1.

Table 1: Name, CAS-number, Structure, Physical-chemical properties of compounds of interest.

Compound	CAS-number	Chemical structure	Phys. Chem.. properties	Analytical method
MEA	141-43-5	H_2N—CH_2—CH_2—OH	Mp: 10,5 bp: 171 pKa: 8,9	IF + LC/MS-ESI TD-GC/MS
AMP	124-68-5	Me—C(NH$_2$)(Me)—CH_2—OH		IF + LC/MS-ESI TD-GC/MS
MDEA	105-59-9	HO—CH_2—CH_2—N(Me)—CH_2—CH_2—OH		IF + LC/MS-ESI TD-GC/MS
Piperazine	110-85-0		Mp: 106 bp: 146 pKa: 9,9	IF + LC/MS-ESI TD-GC/MS
Formamide	75-12-7	H_2N—CH═O		IF + LC/MS-ESI TD-GC/MS
Acetamide	60-35-5	H_2N—C(═O)—CH_3	Mp: 81 bp: 222 pKa: 16,6	IF + LC/MS-ESI TD-GC/MS
Ethanol, 2-(nitroamino)-	74386-82-6	HO—CH_2—CH_2—NH—NO_2	mp: ? bp: 266 pKa: 6,3	IF + LC/MS-ESI

3 Available measurement techniques

Different approaches could be applied for the analysis of amines and their degradation products in air. There are two different approaches for environmental chemical measurements either direct measurements with the measurement instrument placed at the sampling site (on-site or in-field) or alternatively sampling of air or particle sampling at the sampling site, transport to the laboratory and extraction and measurement at the laboratory (off-line).

There are several on-line and in-field techniques available. The instrument with the highest applicability is Proton transfer reaction Time-of-flight mass spectrometry (PTR-TOF-MS) (de Gouw et al., 2007). However, to get optimal output of this instrument a skilled operator must follow the instrument out to the sampling site. Most of the on-site instruments are only suitable for high concentrations which are only found in emissions or very close to the emission source.

With off-line methods, on the other hand, where sampling and analysis are two separate tasks, the sample size can often be increased and lower limits of detection can be achieved. The used sampling techniques are depending on the physical and chemical properties of the analytes, on the necessary limit of detection, and on expected outcome of the measurements. Sampling can be performed as active sampling with an air pump or as passive sampling with a diffusion controlled passive sampling device. Both filters, impregnated filters, different adsorbents, and absorption solutions are relevant sampling media depending on if the analyte is in the gaseous phase or bound to particles. As for sampling the choice of analytical techniques are strongly depending on the physical and chemical properties of the analytes, on the necessary limit of detection, and on expected outcome of the measurements. There is not one method covering all analytes and all possible questions. Most of the methods are coupled methods starting with an extraction or evaporation step, often a clean-up, in many cases a chromatographic separation (gas, liquid, or ion chromatography) and finally instrumental quantification often with mass spectrometry. In Table 2 an overview on analytical instruments available at NILU is given.

Table 2: Analytical instruments available at NILU.

Instrument	Compounds	Comments
2 GC/LRMS with split/splitless injector	Volatiles and semi-volatiles with low to medium polarity	Versatile and easy to run
4 GC/HRMS with split/splitless injector	Volatiles and semi-volatiles with low to medium polarity	Ultimate sensitivity and selectivity
1 GC/MS-MS with split/splitless injector	Volatiles and semi-volatiles with low to medium polarity	Identification of unknowns
1 GC/MS-TOF or GCxGC/MS-TOF with thermo desorption unit or split/splitless injector	Volatiles and semi-volatiles with low to medium polarity	Method of choice for volatiles Identification of unknowns
1 LC/LRMS	Medium to high polarity	
2 LC/MS-TOF	Medium to high polarity	Ultimate sensitivity and high mass resolution Identification of unknowns
1 LC/MS-MS	Medium to high polarity	Identification of unknowns
3 Ion chromatographs	Ions or polar molecules	Cheap method for routine applications

3.1 Sampling techniques

3.1.1 Adsorbent tubes

Air sampling on adsorption tubes (I.D. 4 mm and Length 115 mm) filled with the adsorbent Tenax TA and a sample size of 5 to 100 litres are very often used in a first approach to get an overview about unknown sample composition. They are usually collected by active exposure of the tubes with an air pump. Exposure time can typically be between 10 min and 8 h. Sample tubes have to be cleaned before exposure. There is also the possibility of passive (diffusive) sampling with these tubes − the diffusion rates are comparable to sampling rates of about 30 ml per hour.

3.1.2 Impregnated filters

The first filter in the air stream is an aerosol filter for collecting the airborne particles. This is followed by an acid-impregnated filter for alkaline air components such as NH_3 and different amines. Ammonia and amines are effectively retained on a filter impregnated with citric or oxalic acid. When a 2-filter pack is applied the acid impregnated filter should be the last in the air stream (Figure 1).

A diagram showing the sampling principle is given in Figure 3.2.1. The air intake should have a cylindrical, vertical section 15 cm wide and at least 25 cm high.

This air intake reduce the sampling efficiency for particles larger than 10 µm a.e.d., such as soil dust particles, large sea spray droplets, large pollen, and fog droplets. The filter pack is placed directly in the air intake, and it should have separate supports for the aerosol and the impregnated filters in order to avoid contamination from one filter to the next. An expanded view of a filter pack and its components is shown in Figure 1.

It is important to avoid leaks in the filter pack. The filter pack in Figure 1 should be tightened to the torque specified by the producer. Care should be taken to avoid materials in the filter pack which may be a source of contamination or absorb amines or other air components which are to be determined. Teflon, polyethylene, polypropylene, PVC, and polycarbonate are recommended materials. Ordinary rubber and nylon contains amines and should be avoided.

Figure 1: Filter pack with one aerosol filter and one impregnated filter for gases.

The filter pack should be connected to the sampling line with an airtight seal, using either a nut and gasket, or push-fitted tubing. The sampling line connects the air intake and filter pack to a pump and a gas meter in series. The pump should be a membrane pump of sufficient capacity to allow 15 l/min. against a pressure difference of 10-20 kPA (0.1 atm.), which is the typical pressure drop across two filters. It is essential that the pump is leak proof against outside air in order to allow reliable metering of the air volume at the outlet of the pump. A dry bellows-type gas meter may be used for recording of the air sample volume. This is a relative inexpensive instrument, which is readily available commercially. The accuracy of commercial gas meters is typically within $\pm$ 5%; calibration not less than once or twice a year is therefore mandatory. Better accuracy is obtainable with a wet gas meter. Both devices will record the air volume at the temperature and pressure conditions in the pump. If the pump and gas meter is kept at room temperature, no corrections are usually required, and the air volume is then assumed to be the sample air volume at 20 °C. If deviations of more than $\pm$ 5 °C are expected, the temperature in the gas meter surroundings has to be recorded and the air volume corrected accordingly.

For impregnation of filters the following procedure may be used: The filters are placed on plastic stoppers after which the impregnation solution (0.33 M oxalic acid = 3.0 g oxalic acid, methanol to 100 ml volume) is dripped on the filter. The filters may be dried in air, usually half an hour is sufficient. When the filters are dried, they must be placed in plastic bags and the zippers closed.

A list containing only some of the suppliers of the various types of equipment is given below:

Prefilter for collection of aerosols:
Teflon filter by Gelman, Zefluor 2 µm.

Cellulose filters for impregnation with potassium hydroxide to be used for sampling of sulphur dioxide:
47 mm Whatman 40 (W40) cellulose filter
Whatman International Ltd., Maidstone, England

Filter packs for two or three filters, with clamp and wrench:
NILU Products, P.O. Box 100, NO-2027 Kjeller, Norway

Membrane pump:
GAST, Model DOA-P101-BN
MFG. Corp., Benton Harbor, Mich. USA

Gas meter:
FLONIDAN
Gallus 2000 G1.6
Islandsvej 29
DK-8700 Horsens, Denmark

Mass flow controller:
TYLAN GmbH
Kirchhoffstrasse 8
Eching, Germany

3.2   Chemical analysis techniques

3.2.1   *Thermo desorption coupled with gas chromography/mass spectrometry (TD-GC/MS)*

The samples were analysed on an Automatic Thermo Desorption Unit ATD 400 (Perkin Elmer) coupled to a Hewlett Packard 1800 A GCD gas chromatography/mass spectrometry (GC/MS) system. Tubes were desorbed at 275°C for 20 min, preconcentrated at -30°C and separated on J&W DB1701 capillary column (30 m×0.22 mm×1.0 μm). The mass spectrometer was used in full scan mode with a mass range 33 to 450 amu. The quantification was performed with external standards on pre-cleaned tubes.

3.2.2   *Filter extraction and liquid chromatography/mass spectrometry (LC/MS)*

After dismantling the filter pack the aerosol filter and the acid-impregnated filter are extracted by 10 mL deionized water in an ultra-sonic bath for about 30 min. After extraction the solutions are centrifuged to separate undissolved particles and are ready for LC/MS analysis.

Quantification was performed on an Agilent 1100 liquid chromatography system (Agilent Technologies, Waldbronn, Germany), equipped with an auto-sampler, a quaternary pump, an on-line degassing system and a diode array detector (UV). The compound separation was performed using a reversed phase C18 column (Atlantis dC18, 2.1 mm ID × 150 mm length, 3 μm, Waters, Milford USA). A stainless steel inlet filter (Supelco, 0.8 μm) was used in front of a pre-column with the same stationary phase as the separation columns. The analytical detector was a Micromass LCT orthogonal-acceleration time-of-flight (TOF) mass spectrometer (MS) equipped with a Z-spray electrospray ion source and a 4 GHz time to digital converter (TDC) (Micromass Ltd, Wythenshawe, Manchester, UK).

The gradient elution was performed with 0.075% formic acid in water and 0.075% formic acid in acetonitrile. The binary gradient had a flow rate of 0.2 mL/min. A gradient elution from 100% acidified water to 99% acidified methanol over 22 min separated all compounds. The flow then remained isocratic until 32 min. At 32.5 min the setting was 100 A and the column was equilibrated up to a runtime of 40 min, with increased flow rate (0.5 mL/min). The analytical detector was operated in positive ion mode and the electrospray source parameters were optimised to the following values; sample cone cycling 20/30 V, capillary voltage 2.8 kV, extraction cone 3 V, source temperature 130 °C, desolvation temperature 350 °C, cone gas flow 24 L/h and desolvation gas flow 600 L/h. The pusher frequency was operated in automatic mode. The data processing and instrument (HPLC-HRMS) control were performed by the MassLynx software, and quantification was performed with signal extraction of a peak width of 90 amu (typical).

4   Results

4.1   TD-GC/MS

Since no real environmental samples containing the compounds of interest have been made available several indoor and outdoor air samples containing similar compounds were analysed. The method has also been used for several hundreds of samples from industrial processes like paper-industry (Borregaard, Norske Skog) vulcanisation processes (Swedala, Sweden), fermentation plants (Alpharma), paint-industry (Jotun) and incineration plants. The method is also extensively used in emission studies from building materials. In samples taken from vulcanisation processes even volatile amines are analysed with this method. In all these studies at least the 30 compounds with highest concentrations were successfully identified in some cases even up to hundred different compounds.

Electron impact spectra obtained by analysing pure standards of MEA, AMP, MDEA, piperazine, formamide, and acetamide are shown in Figure 2.

The limit of detection (LoD) is dependent on a lot of different factors like sample volume, recovery rate, chromatographic separation, interfering compounds, instrumental sensitivity, and the response factor of a given compound. For TD-GC/MS which is normally performed with electron impact ionization in full scan modus, the individual response factors do not vary much from compound to compound. Therefore, a normal procedure in samples with unknown composition is to extrapolate response factors from one compound to another. This is an accepted method, however, measurement uncertainty is higher than for a quantification based on isolated standards with known concentrations.

A typical LoD for ambient air samples is in the range of $1 - 100$ ng/m^3. In smoke stack samples with a smaller sample volume LoD is expected to be around $0,1 - 10$ µg/m^3. The numbers are based on about 10 000 samples of ambient air and about 2 000 samples of emissions from industrial processes.
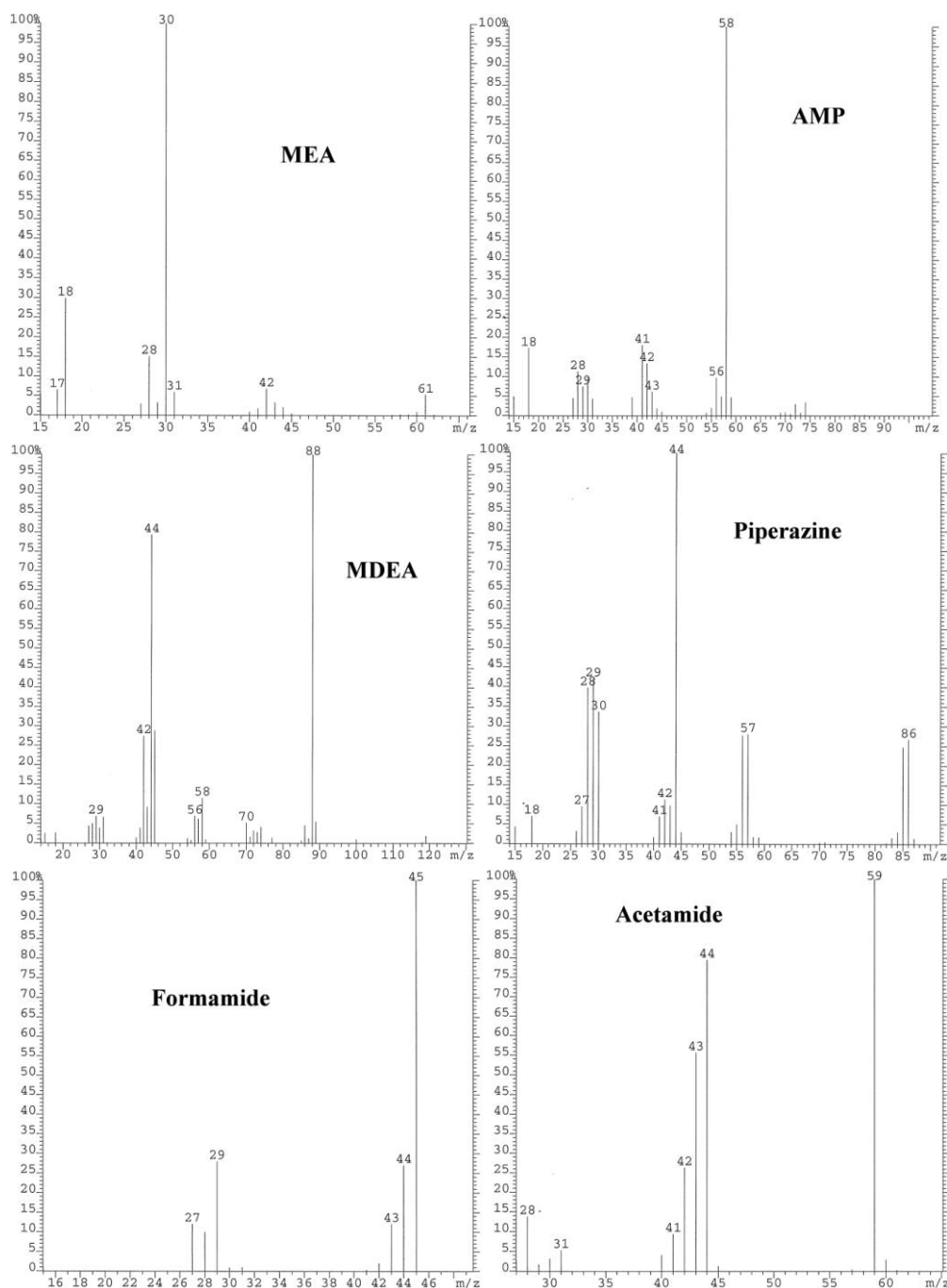
Figure 2: Electron impact spectra of MEA, AMP, MDEA, piperazine, formamide, and acetamide.

4.2 IF LC/MS

Since no real environmental samples containing the compounds of interest have been made available, the method was tested by spiking filters with pure standards of MEA, AMP and piperazine. The test chromatograms and typical spectra are shown in Figure 3 to Figure 6.
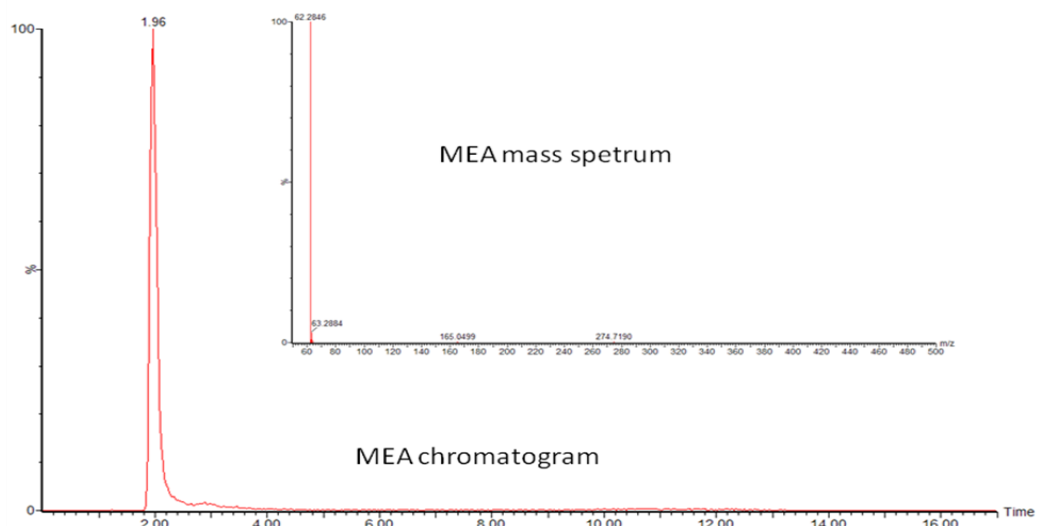
.

Figure 3: Selected ion mass chromatogram and electrospray ionization mass spectra of MEA.
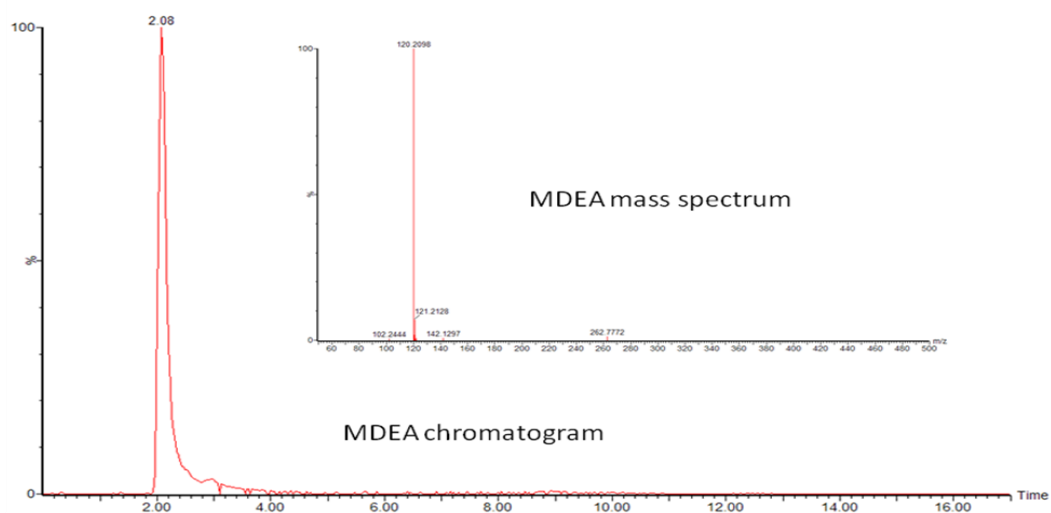

Figure 4: Selected ion mass chromatogram and electrospray ionization mass spectra of MDEA.
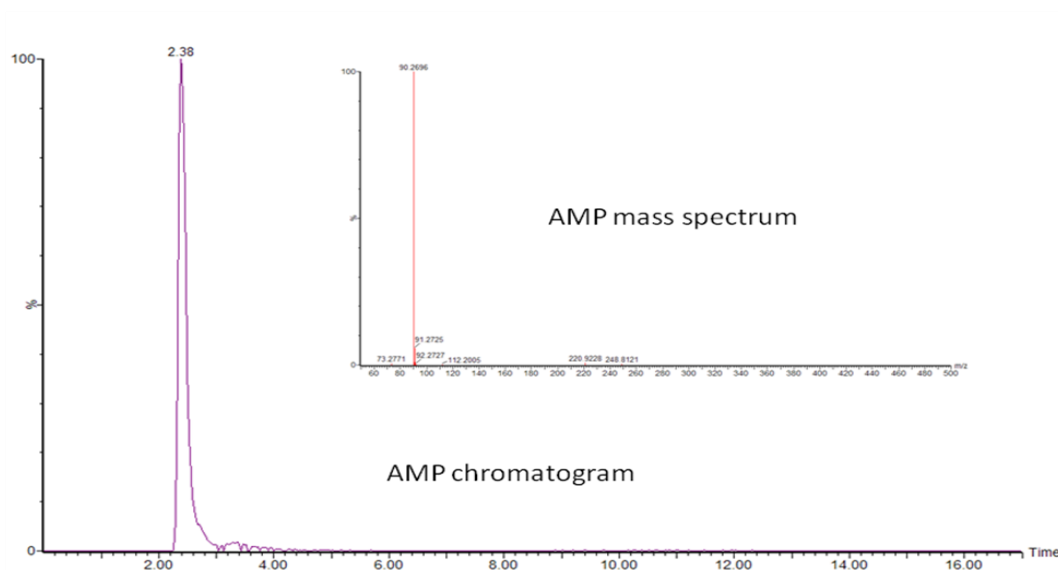
Figure 5: Selected ion mass chromatogram and electrospray ionization mass spectra of AMP.
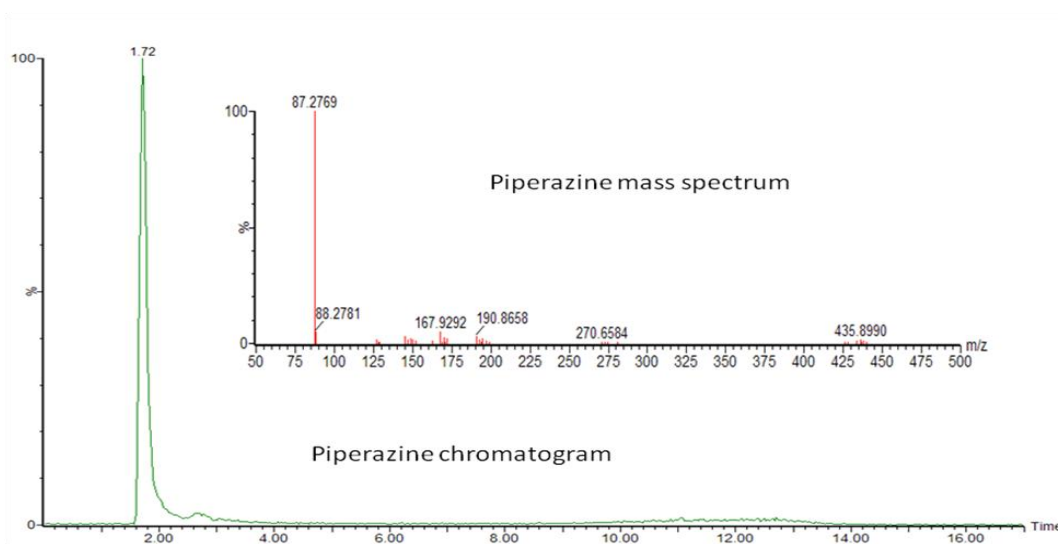

Figure 6: Selected ion mass chromatogram and electrospray ionization mass spectra of piperazine.

The limit of detection (LoD) is dependent on a lot of different factors like sample volume, recovery rate, chromatographic separation, interfering compounds, instrumental sensitivity, and the response factor of a given compound. In addition, for LC/MS the situation is even more complicated due to the ionisation principles and the chemical structure dependency. LC/MS are normally using soft ionization methods as electrospray or atmospheric pressure chemical ionization. The response factor for these methods is extremely influenced by the structure of the measured compounds and the sample matrix. The electronic effects of functional groups like amines or carboxylic acid groups can change the ionization capability completely. It is therefore not possible in LC/MS to extrapolate response factors as it is possible for GC/MS in electron impact mode.

Based on the instrumental sensitivity obtained in the experiments performed in this work for MEA,AMP,MDEA and piperazine, combined with the experience from previous work (Dye, 2006; Wiklund, 2008) a typical LoD for ambient air samples is expected to be found in the range of $1 - 100$ ng/m^3. In smoke stack samples with a smaller sample volume LoD is expected to be around $0,1 - 10$ µg/m^3. Due to the sample matrix dependency the use of real stack samples and samples from plant areas are necessary to provide more specific LoDs for the LC/MS analysis.

5 Discussion

During this initial test phase two complimentary analytical methods, TD-GC/MS and IF LC/MS have been evaluated. The evaluation indicates that both methods can give important information on the existence and concentration of compounds directly emitted or secondarily formed by the CO_2 capture process. However, to proof this we need access to the real stack samples and samples close to emission sources.

5.1 TD-GC/MS

The three major advances of the TD GC/MS method are (1) separation capacity, (2) library identification, and (3) quantification.

In this phase we used only 1-dimensional GC separation which already allows to separate up to 250 different compounds and identification of up to 100 compounds. This may be extended to up to 1000 different compounds when using 2-dimensional GC technology (GCxGC/TOF) which is also available at NILU's laboratories.

For GC/MS in electron impact mode, more than 100 000 different spectra are available in spectra libraries. This allows a very quick and effective structural identification of many compounds. Compounds where no spectrum is stored in the library, can be identified by interpretation of the mass spectrum and its fragmentation pattern.

Compared to other methods the response factors of the different compounds analyzed with GC/MS in EI mode are not varying too much and allow a semi-quantitative estimation of the concentrations of all identified compounds even if no isolated standard compound is available. With isolated standard compounds this method can become fully quantitative and fully validated.

The major drawback of GC-methods are their weakness towards the separation of polar compounds, which means that separation and analysis of substituted amines is on the edge of what is possible by gas chromatography. Since the principle of gas chromatography requires analytes in the gas phase, this method is in no case applicable for thermo-labile compounds. The areas of applicability of TD-GC/MS and IF LC/MS are shown schematically in Figure 7.
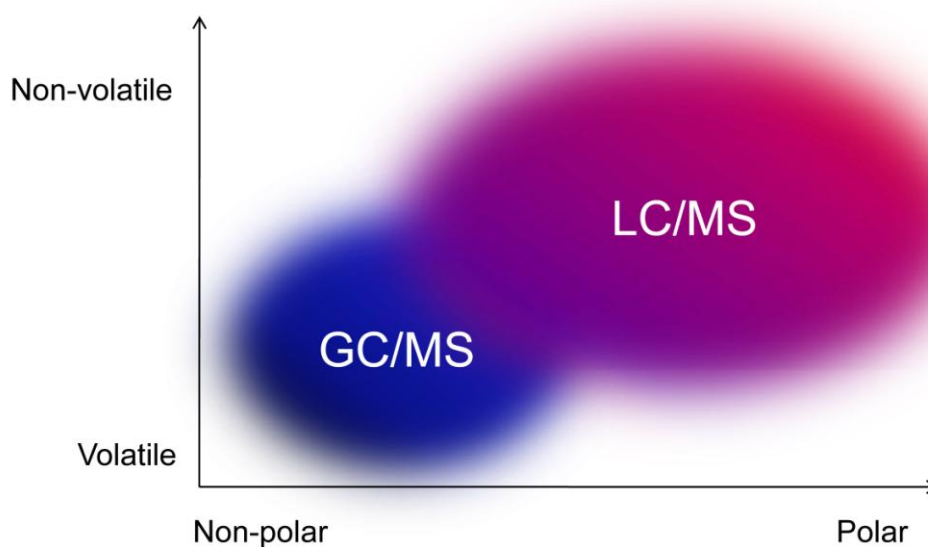
Figure 7: Areas of applicability of GC/MS and LC/MS given by Waters Corp.

In table 3 the current status and risk of failure for the different methods of analysis for the different compounds and compound groups are summarized.

Table 3: Status and Risk of failure for TD-GC/MS analysis of different compound groups.

Methods	Compound groups	Status	Risk of failure
Analysis of mother compounds	MEA, MDEA, AMP, piperazine and other amines	Initially tested and will probably be available 6 - 8 weeks after contracting	Medium
Analysis of degradation compounds available as isolated standard material		Not tested, but will probably be available 8 – 12 weeks after purchase of the isolated standard material	Significant
Analysis of degradation compounds NOT available as isolated standard material		May be possible but with the following unknowns: • Analyte stability • Reactivity • Quantification is possible but difficult.	High

5.2   IF LC/MS

LC/MS, contrary to TD-GC/MS, has been shown to be very suitable for polar compounds, even for thermo-labile substances. The limiting prerequisites for LC/MS analysis are that the analytes are soluble, stabile in solution and ionizable

within the ion source of the LC/MS instrument. As the compounds under LC/MS conditions do not fragment significantly, the mass spectra are very simple without much structural information. Therefore, the use of libraries for identification is very limited. However, a time-of-flight type LC/MS can be run in high resolution mode which in many cases can give the sum formula of the compound. The sum formula together with information obtained by induced fragmentation and retention time is often enough to identify a compound.

The most important drawback of LC/MS is that the response factor can vary several orders of magnitude from one compound to another. Furthermore, coeluting compounds may cause suppression of the analyte signal. This means that the method must be calibrated and validated with isolated standards for quantification.

In Table 4 the current status and risk of failure for the different methods of analysis for the different compounds and compound groups are summarized.

Table 4: Status and Risk of failure for IF LC/MS analysis of different compound groups.

Methods	Compound groups	Status	Risk of failure
Analysis of mother compounds	MEA, MDEA, AMP, piperazine and other amines	Initially tested and will probably be available 6 - 8 weeks after contracting	Very small
Analysis of degradation compounds available as isolated standard material		Not tested, but will probably be available 8 – 12 weeks after purchase of the isolated standard material	Significant
Analysis of degradation compounds NOT available as isolated standard material		May be possible but with the following unknowns: • Analyte stability • Reactivity • Quantification is not possible.	High

5.3 Strategy for finalization of method development

In the planned Phase II of this analytical method development, given that the necessary chemicals or facilities are available, the analytical screening methods will be fully verified and the quality of the methods will be validated. Furthermore, a decision will be made on which method to use for the different compounds taking into account the pros and contras for the two complementary methods TD-GC/MS and IF LC/MS see Figure 7.

NILU has one of the most advanced and best equipped environmental analytical laboratories in the Nordic countries with 4 GC/HRMS, 5 GC/LRMS, 1

GCxGC/MS-TOF, 1 GC/MS-MS, 3 LC/MS-TOF, 1 LC/LRMS, and 2 ICPMS. The organic group consisting of about 10 senior scientists together with engineers and technicians, has over the last few years performed a lot of extremely demanding screening projects for national and international environmental pollution authorities. Typical for these studies is the fact that in the phase of planning and contracting not all methods are completely established and validated. In most cases the analyst has only some ideas how to solve the problem. NILU has also performed a lot of studies for industrial customers where the composition of the samples was totally unknown in the initial phase of the study. Most screening studies have a starting point with much more unknowns as knowns. (Andersson, 2005 and 2006; Dye, 2006; Fjeld 2004 and 2005; Kaj 2005 and 2007; Schlabach, 2007; Thomas, 2007; Woldegiorgis 2005, 2006, and 2007). Before starting work on contracted samples, tested and accepted methods are finally validated with "real world" samples of the same type of matrix. The validation includes normally field and method blanks, spiking and recovery tests, stability tests and, in some cases, laboratory intercalibrations.

The Phase I study showed that the described methods are working well for potential mother compounds like MEA, AMP and piperazine in artificial air samples and it is expected that the final validation can be performed without major problems. Furthermore, similar methods have also successfully been applied to other more complex amines like benzothiazoles (Dye, 2006) and different amine-containing pharmaceuticals (Andersson, 2006, and Woldegiorgis, 2007).

5.4 Open questions

In Table 5 open questions and possible actions to these questions are summarized.

Table 5: Questions to be solved before acceptance of the different analytical methods.

Question	Action
Analyte stability as:	
Thermolability	Spiking of filters or adsorbents with analyte and storing under different conditions
Photodegradation	
Reaction with O_3 and NO_x	
Quantification/LoD	Purchase or synthesis of standard material

5.5 Other matrices

In this initial study focus was on air samples and no other matrix type has been tested. With our experience from other method development projects we believe that it will be possible to adjust the TD-GC/MS method to both water and solid samples like soil or sediment. However, the LC/MS must be adapted and tested for each new type of matrix since interfering compounds can cause severe suppression problems.

6 References

Akyuz, M. (2008) Simultaneous determination of aliphatic and aromatic amines in ambient air and airborne particulate matters by gas chromatography-mass spectrometry. *Atmos. Environ. 42,* 3809-3819.

Andersson, J., Woldegiorgis, A., Remberger, M., Kaj, L., Ekheden, Y., Dusan, B., Svenson, A., Brorström-Lundén, E., Dye, C. and Schlabach, M. (2006) Results from the Swedish national screening programme 2005. Subreport 1: Antibiotics, anti-inflammatory substances and hormones. Göteborg, Swedish Environmental Research Institute (IVL report B1689).

Bråten, H.B., Bunkan, A.J., Bache-Andreassen, L., Solimannejad, M. and Nielsen, C.J. (2008) Final report on a theoretical study on the atmospheric degradation of selected amines Oslo. Kjeller (NILU OR 77/2008).

Dye, C., Bjerke, A., Schmidbauer, N. and Manø, S. (2006) Måling av luftforurensning i innendørs kunstgresshaller. Kjeller (NILU OR 03/2006).

Dye, C., Remberger, M., Kaj, L. and Schlabach, M. (2006) Determination of tetracyclines in the sewage sludge using high performance liquid chromatography combined with time of flight mass spectrometry. Kjeller (NILU PP 22/2006).

Fjeld, E., Schlabach, M., Berge, J.A., Eggen, T., Snilsberg, P., Källberg, G., Rognerud, S., Enge, E.K., Borgen, A. and Gundersen, H. (2004) Kartlegging av utvalgte nye organiske miljøgifter – bromerte flammehemmere, klorerte parafiner, bisfenol A og triclosan. Oslo, NIVA (Statlig program for forurensningsovervåking. Rapport 895/2004).

Fjeld, E., Schlabach, M., Berge, J.A., Green, N., Eggen, T., Snilsberg, P., Vogelsang, C., Rognerud, S., Kjellberg, G., Enge, E.K., Dye, C., Borgen, A. and Gundersen, H. (2005) Kartlegging av utvalgte nye organiske miljøgifter 2004: bromerte flammehemmere, perfluoralkylstoffer, irgarol, diuron, BHT og dicofol. Oslo, NIVA (Statlig program for forurensningsovervåking. Rapport 927/2005).

Fournier, M., Lesage, J., Ostiguy, C. and Van Tra, H. (2008) Sampling and analytical methodology development for the determination of primary and secondary low molecular weight amines in ambient air. *J. Environ. Monit., 10,* 379-386.

Gouw, J. de, Warneke, C., Karl, T., Eerdekens, G., Veen, C. van der and Fall, R. (2007) Measurement of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectr. Rev., 26 ,* 223-257.

Green, N., Dye, C., Remberger, M., Schlabach, M., Herzke, D., Schøyen, M., Bakke, T., Huber, S., Uggerud, H.T., Brevik, E.M., Plosz, B. and Vogelsang, C. (2008) Screening of selected metals and new organic contaminants 2007.

Phosphorus flame retardents, polyfluorinated organic compounds, nitro-PAHs, silver, platinum and sucralose in air, wastewater treatment facilities, and freshwater and marine recipients. Oslo, NIVA (Statlig program for forurensningsovervåking. Rapport 1014/2008).

Kaj, L., Ekheden, Y., Dusan, B., Hansson, K., Cousins, A.P., Remberger, M., Brorström-Lundén, E. and Schlabach, M. (2007) Screening 2004 – uppföljningsprojekt. Analys av oktaklorstyren, flyktiga metylsiloxaner, vissa fenoler och endosulfan. Göteborg, Swedish Environmental Research Institute (IVL report B 1745)

Kaj, L., Schlabach, M., Andersson, J., Cousins, A.P., Schmidbauer, N. and Brorström-Lundèn, E. (2005) Siloxanes in the Nordic environment. Copenhagen, Nordic Council of Ministers (TemaNord 2005:593).

Knudsen, S., Moe, M.K., Schlabach, M., Schmidbauer, N. and Dye, C. (2008) Environmental impact of amines from CO2 capture. Kjeller (NILU OR 52/2008).

Rabaud, N. E., Ebeler, S. E., Ashbaugh, L.L. and Flocchini, R.G. (2003) Characterization and quantification of odorous and non-odorous volatile organic compounds near a commercial dairy in California. *Atmos. Environ., 37,* 933-940.

Rampfl, M., Mair, S., Mayer, F., Sedlbauer, K., Breuer, K. and Niessner, R. (2008) Determination of primary, secondary, and tertiary amines in air by direct or diffusion sampling followed by determination with liquid chromatography and tandem mass spectrometry. *Environ. Sci. Technol., 42*, 5217-5222.

Schlabach, M., Andersen, M.S., Green, N., Schøyen, M. and Kaj. L. (2007) Siloxanes in the environment of the inner Oslofjord. Kjeller (NILU OR 27/2007).

Thomas, K.V., Dye, C., Schlabach, M. and Langford, K.H. (2007) Source to sink tracking of selected human pharmaceuticals from two Oslo city hospitals and a wastewater treatment works. *J. Environ. Monit., 9*, 1410-1418.

Wiklund. P., Woldegiorgis, A., Remberger, M., Kaj, L., Viktor, T., Lilja, K., Brorström-Lundén, E. and Dye, C. (2008) Results from the Swedish national screening programme 2007, Subreport 1: Amines. Göteborg, Swedish Environmental Research Institute (IVL-Report in press).

Woldegiorgis, A., Andersson, J., Brorström-Lundèn, E., Kaj, L., Remberger, M., Ekheden, Y., Dusan, B., Svensson, A., Dye, C. and Schlabach, M. (2007) Screening of selected pharmaceuticals in Sweden. In: *2nd EMCO workshop on emerging contaminants in wastewaters: monitoring tools and treatment technologies.* 26-27 April, Belgrade, Serbia. Book of abstracts. p. 64.

Woldegiorgis, A., Andersson, J., Remberger, M., Kaj, L., Ekheden, Y., Blom, L., Brorström-Lundén, E., Borgen, A., Dye, C. and Schlabach, M. (2006) Results

from the Swedish national screening programme 2005. Subreport 3: Perfluorinated alkylated substances (PFAS). Göteborg, Swedish Environmental Research Institute (IVL report 1698).

Woldegiorgis, A., Green, J., Remberger, M., Kaj, L., Brorström-Lundén, E., Dye, C. and Schlabach, M. (2006) Results from the Swedish screening 2006. Subreport 4: Pharmaceuticals. Göteborg, Swedish Environmental Research Institute (IVL report 1751).

Norwegian Institute for Air Research (NILU)

P.O. Box 100, N-2027 Kjeller, Norway

Associated with CIENS and the Environmental Research Alliance of Norway
ISO certified according to NS-EN ISO 9001

TITLE Evaluation of analytical methods for amine related emissions and degradation products in emission and ambient air Phase I	PROJECT LEADER Svein Knudsen
	NILU PROJECT NO. N-108068

AUTHOR(S) Christian Dye, Norbert Schmidbauer, and Martin Schlabach	CLASSIFICATION * A
	CONTRACT REF. Erik Gjernes, Gassnova SF Merethe Sjøvoll, StatoilHydro ASA Rehan Naqvi, Shell Technologies Norway AS

REPORT PREPARED FOR
Gassnova SF,
StatoilHydro ASA
Shell Technology Norway AS,

ABSTRACT

This report describes the chemical analysis methods evaluated and available for chemical screening of the CO_2 capture process. The methods are designed to cover the entire chemical range of compounds by using several specialized sampling and analysis techniques.

Both experience from other technical processes using amines for CO_2 capture, literature survey and own theoretical evaluations revealed different chemical compounds as potential pollutants from CO_2 capture process at natural gas power plants: amines, substituted amines, amides, nitramines and nitrosamines.

During this initial test phase, two complementary analytical methods have been tested: (1) exposure of adsorbent tubes followed by thermo desorption and analysis by gas chromatography and mass spectrometry (TD-GC/MS) and (2) exposure of impregnated filters followed by extraction and analysis by liquid chromatography and mass spectrometry on a time-of-flight instrument (IF + LC/MS). For both methods real samples and some spiked samples have been used for testing. Both methods can give important information on the existence and concentration of compounds directly emitted or secondarily formed by the CO_2 capture process.

NORWEGIAN TITLE

Evaluering av analytiske metoder for aminrelaterte utslipp og nedbrytningsprodukter i utslipp og i luft.

KEYWORDS		
CO_2 capture	Amines	Chemical analysis

ABSTRACT (in Norwegian)

Denne rapporten beskriver kjemiske målemetoder som er tilgjengelige og evaluerte med hensyn på problemstillinger som faglig ligger nær det å bestemme utslipp fra CO_2-fangst. Metodene er designet til å favne vidt over mange kjemiske komponentklasser ved bruk av spesialisert prøvetakingsteknikk og analyseutstyr.

I rapporten er det lagt til grunn erfaringer fra aminprosesser knyttet til CO_2-fangst og det er utført en litteraturgjennomgang og en prosjektrelatert teoretisk studie. Dette arbeidet viste at det finnes et potensial for utslipp av forurensinger fra aminbasert teknologi: aminer, substituerte aminer, amider, nitraminer og nitrosaminer.

I løpet av denne innledende fasen har to komplementære analysemetoder blitt testet: (1) eksponering av adsorbsjonsrør med påfølgende termodesorbering og kjemisk analyse med gasskromatografi og massespektrometri (TD-GC/MS) og (2) eksponering av impregnerte filter med påfølgende væskeekstraksjon og kjemisk analyse med høytrykks væskekromatografi og massespektrometri (IF+LC/MS).

Spikede syntetiske prøver har blitt benyttet i uttestingen. Begge metodene kan gi viktig informasjon om forekomst og konsentrasjon av både primære og sekundære komponenter i utslipp fra aminbasert CO_2-fangst.