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SUMMARY

The scope of this task was to test and finally create analytical methods for solvent amines and their degradation products possibly present in CO_2-capture unit. Several components with potential environmental impact have been identified among the decomposition products of solvent amines. The work is based on the literature survey of the subtask 4 and the background knowledge of the amine analysis of Ramboll Analytics. N-nitrosamines, low molecular weight (LMW) alkylamines and solvent amines were the main focus of this task. Analytical methods for LMW amides, aldehydes and ammonia were also to be researched. The matrices of interest were the treated flue gas from the absorber column (flue gas), the wash water from the absorber top (wash water) and the rich and lean aqueous amine solution circulating in the absorber (rich/lean amine solvent).

Two separate methods were established for the **nitrosoamine** analysis. First method is bassed on liquid-liquid extraction combined with GC-MS analysis. It is suitable for NDMA, NDEA, NMOR, NPIP and 1,4-dinitrosopiperazine. Detection limit at this point was about 1 ng/l from wash water and 10 ng/l solvent amines, however, lower detection limits are possible. Other method utilizing UPLC-MS/MS technique was developed for the NDELA and N-nitrosopiperazine . The detection limit for NDELA is at 5 % MEA matrix about 50 ng/l (about 350 ng/l at 35 % solvent amine). Group method for nitrosamines was explored. For volatile nitrosamines GC-MS multi-ion analysis (SCAN) combined with mass spectrum library search is applicable. However it is not selective only for nitrosamines.

For the **solvent amines** analysis was performed by direct injection to UPLC-MS/MS or injection after dilution by water. The instrument detection limits (IDL) for solvent amines was found to be 5-10 µg/l, except for piperazine and EDA (IDL's 300 µg/l and 1 000 µg/l). The concentration step is possible but not evaluated detailed at this work, because expected relatively high concentration of solvent amines.

From blank water matrix IDL for the **alkylamines** was found to be 10 µg/l. With preconsentration factor of 200 the MDLs in a sample is around 0.05-0.1 µg/l. The difficulties were observed when concentration step was employed with the sample including five percent of solvent amine. Different concentration methods were tested, such as SPE, LLE, purge and trap and ion pair without success. However, there was some good signs on purge and trap tests. Due to high volatility of alkylamines and inconvenience on concentration step, derivatization of alkyamines on sampling should be evaluated. At this study alkylamines were analysed by UPLC-MS/MS.

For **Formaldehyde and acetaldehyde** analysis DNPH derivatization was used. It was proved to be selective only for aldehydes and insensitive for amine concentration involved in matrix. Detection limit at this point was reached to 50 µg/l both washwater and solvent amines. If lower detection limits are needed, LLE concentration steps may be involved.

Also HS-GC-MSD method for acetaldehyde and heavier aldehydes were tested, but further tests were not performed due to lack of need and relatively high interference with solvent amines.

Ammonia analysis was tested with IC and derivatization followed by GC-MS analysis. IC tests were not fully evaluated within this time frame. However it works with blank water while high concentration of solvent amines causes co-elution and merged peaks related problems.

Ammonia was also analysed by derivatization and analysis by GC-MS. Method is also suitable for solvent amine concentrated samples. Detection limit at this point was about 1 mg/l. Lower detection limits may be obtained after detailed method development.

Tests for **Amides** were performed by GC-MS, UPLC-MS/MS and HPLC-RI. Only HPLC-RI gave response for the target amides in a blank water matrix. When MEA was involved as a solvent amine, no amides were observed.

Further work to optimize methods, acquire lower detection limits and perform large validation is recommended. Also tests for the sorbent materials used at emission measurement and referred at the subtask 2 should be established. It is important to take account the effect of relatively high

concentration of solvent amines during flue gas sampling. During the tests with SPE cartridges it was observerd that high concentration of solvent amine reduces significantly the retention volume of the absorbent. Also tests should include the impact of flue gas components and degradation.

Summary of methods developed during Subtask 5

	Flue gas sample/condensate*	***Wash water (including 5 % of MEA)***	***Solvent amine (including 35 % of MEA***
Nitrosoamines	x	x	x
Nitrosoamines, group method	Only for volatile	Only for volatile	Only for volatile
Alkylamines	x	-	-
Solvent amines	x	x	x
Amides	T&R	-	-
Aldehydes	x	x	x
Ammonia	T&R	-	-

**conctaining only trace amounts of solvent amines*
T&R= tested, observed response, method established but not developed further due to prioritization

List of symbols and abbreviations

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

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1. INTRODUCTION

Carbon dioxide capture from large point sources, such as power plants and industrial facilities, is one way to reduce CO_2 emissions. CO_2 capture through absorption in aqueous solutions of amines, usually alkanolamines, is one of the technologies that are closest to being operational.

Carbon dioxide capture plants will be similar to the units commonly used in the oil industry for the removal of CO_2 and H_2S from natural gas. The absorption takes place in an absorption tower, were CO_2 is removed from the gas stream by means of an aqueous solution of amines circulating countercurrently. Several amines, mostly alkanolamines, are used as solvent amines in gas sweetening units. The rich amine solution from the absorber bottom is cleaned from carbon dioxide in a stripper unit. The lean amine solution from the stripper bottom is then recirculated back to the absorber. The treated gas stream exits from the top of the absorber through a water wash and is emitted to the atmosphere. The solvent amines are susceptible for decomposition during the process. The degradation products accumulate in the absorber, are removed by the wash water or leave the absorber with the treated gas and are emitted to the atmosphere. Several chemical compounds with environmental impact were identified among the products of degradation of solvent amines.

The purpose of this sub-task is to create methods of analysis for solvent amines and their degradation products formed in amine-based CO_2-capture processes. The components of special interest are N-nitrosamines and low molecular weight (LMW) alkylamines. Analytical methods will also be created for solvent amines, LMW amides, aldehydes and ammonia. The sample matrices are the treated flue gas from the absorber column, the wash water from the absorber top and the rich and lean aqueous amine solution circulating in the absorber. Methods are designed keeping the applicability of the analysis of flue gas samples in mind. Sampling methods are described in more detailes at subtask 2.

All the compounds have been treated as trace compounds, with the exception of the solvent amines in rich/lean amine solvent. For N-nitrosamines, not only quantitative but also screening and group methods will be included in this work, but the work has been started with a quantitative method. The work is based on the literature survey of subtask 4 and the background knowledge of the amine analysis by Ramboll Analytics.

2. COMPOUNDS OF INTEREST AND THEIR PROPERTIES

The compounds of interest in this study are the amines present in the unit as solvent and their degradation products. The compounds are divided according to the chemical groups and are listed in alphabetical order within each group (Table 1).

Table 1 Compounds and their properties.

Compound	CAS-number	Formula	MW (g/mol)	T_b (°C)	Water solubility	Reference
Nitrosamines						
1,4-Dinitrosopiperazine	140-79-4	$C_4H_8N_4O_2$	144.13	158	miscible	(Gangolli 2005)
N-nitrosodiethanol-amine (NDELA)*	1116-54-7	$C_4H_{10}N_2O_3$	134.1	114	1 g/l / miscible	(Gangolli 2005, Bingham et al. 2001, Verschueren 2001, Prager 1998)
N-nitrosodiethylamine (NDEA)*	55-18-5	$C_4H_{10}N_2O$	102.1	177	soluble in water 100 mg/l (ca.)	(Gangolli 2005, Bingham et al. 2001, Verschueren 2001, Lewis 2004)
N-nitrosodimethyl-amine (NDMA)	62-75-9	$C_2H_6N_2O$	74.08	154	miscible / infinite	(Bingham et al. 2001, Wypych 2008)
N-nitrosomorpholine (NMOR)*	59-89-2	$C_4H_8N_2O_2$	116.1	224	miscible	(Gangolli 2005, Verschueren 2001)
N-Nitrosopiperazine*	5632-47-3	$C_4H_9N_3O$	115.16	85-95	more soluble in water than NMOR	(Lewis 2004, Garcia et al. 1970)
N-nitrosopiperidine (NPIP)	100-75-4	$C_5H_{10}N_2O$	114.15	100	77 g/l	(Gangolli 2005, Bingham et al. 2001, Verschueren 2001)
Alkylamines						
Diethylamine (DEN)*	109-89-7	$C_4H_{11}N$	73.14	55	miscible / 815 g/l at 14 ºC	(Verschueren 2001, Wypych 2008, Dean 1999)
Dimethylamine (DMA)*	124-40-3	C_2H_7N	45.08	7	very soluble in water /miscible, saturated / 24 % at 60 ºC	(Verschueren 2001, Lewis 2004, Dean 1999, Pohanish 2008)
Ethylamine (EA)*	75-04-7	C_2H_7N	45.1	16	miscible	(Wypych 2008)
Methylamine (MMA)*	74-89-5	CH_5N	31.07	-6	1 000 g/l	(Wypych 2008)
Triethylamine (TEA)*	121-44-8	$C_6H_{15}N$	101.22	89	170 g/l	(Wypych 2008)
Trimethylamine (TMA)*	75-50-3	C_3H_9N	59.11		miscible / 48 % at 30 ºC	(Bingham et al. 2001, Verschueren 2001, Pohanish 2008)
Solvent amines						
2-amino-2-methyl-1-propanol (AMP)	124-68-5	$C_4H_{11}NO$	89.14	165	miscible	(Wypych 2008, Knovel 2003, Yaws 2010)
Diethanolamine (DEA)	111-42-2	$C_4H_{11}NO_2$	105.14	269	infinite	(Wypych 2008)
1,2-diaminoethane (EDA)	107-15-3	$C_2H_8N_2$	60.1	116	miscible	(Wypych 2008)
N-methyldiethanol-amine (MDEA)	105-59-9	$C_5H_{13}NO_2$	119.16	245	miscible	(Lewis 2004, DIPPR)
Monoethanolamine (MEA)	141-43-5	C_2H_7NO	61.08	171	miscible	(Verschueren 2001, Wypych 2008)

Compound	CAS-number	Formula	MW (g/mol)	T_b (°C)	Water solubility	Reference
Piperazine	110-85-0	$C_4H_{10}N_2$	86.14 (anhydr.)	146 (anhydr.)	soluble 150 g/l at 20°C and pH 12	(Bingham et al. 2001, Institute for Health and Consumer Protection European Chemicals Bureau. 2005)
Amides						
Acetamide	60-35-5	C_2H_5NO	59.1	222	2 000 g/l	(Wypych 2008)
Formamide	75-12-7	CH_3NO	45.04	210	infinite / miscible	(Verschueren 2001, Wypych 2008, Dean 1999)
Aldehydes						
Acetaldehyde	75-07-0	C_2H_4O	44.06	21	infinite	(Wypych 2008)
Formaldehyde	50-00-0	CH_2O	30.03	-21 (gas)	soluble, 400 g/l	(Wypych 2008)
Others						
Ammonia	7664-41-7	NH_3	17.03 (anhydr.)	-33 (gas)	600 g/l (15 °C)	(MSDS 2005)

*Priority compounds

3. SAMPLE MATRICES

3.1 Treated flue gas (gaseous)

The compounds of interest will be analyzed in the treated flue gas from the head of the absorption tower. The flue gas undergoes water wash before the sampling point. The flue gas is at a temperature between 25 – 50 °C with possible presence of water droplets and various particles. A tentative composition of the gas is given in Table 2. The concentration of both process amines and their degradation products are expected to be at ppm level.

Table 2 Tentative specifications of the treated flue gas

Composition	Specification	Units
Oxygen	15	mol-%
Nitrogen	81.5	mol-%
Carbon Dioxide	0.5	mol-%
NO_x	n.a.	
NO_2	n.a.	
NH_3	<50	ppmv
SO_2	n.a.	
Water	3	mol-%
Amines	<5	ppmv

n.a. – not available

3.2 Wash water from the absorber tower (liquid)

The treated flue gas undergoes water wash before being emitted to the atmosphere. The water wash reduces the emissions of process amines and other undesirable compounds. The sample will consist mostly of water. Process amines and their degradation products are expected to be present in trace amounts. However, due to high concentration of solvent amines involved in captore process, solvent amines are expected to find at relatively higher concentrations from the washwater. In addition, the wash water and fluegas condensate during emission measurements are expected to be similar at the chemical composition. Solvent amines are expected to be found at 0-5 % concentration levels. At the current work concentrations of 2 % or 5 % of MEA was used to test effect of matrix.

3.3 Rich and lean amine solvent (liquid)

The aqueous amine solution absorbs CO_2 from the gas under treatment by flowing countercurrently to the gas in the absorber unit. The difference between rich and lean solvents is in the amount of CO_2 absorbed. The rich amine solution comes from the bottom of the absorber and it is rich in CO_2. The lean solution comes from the top of the stripper, where CO_2 was stripped, and it is re-circulated to the absorber. The main components of these samples will be water and the process amines. Some examples of possible solvents are given in Table 3. The amine degradation products will be present in traces.

Table 3 Examples of aqueous solvents

		Main amine	Secondary compound
Solvent A	Water (69 wt%)	MEA (30 wt%)	Heat stable salts (1 wt%)
Solvent B	Water (60 wt%)	AMP (25 wt%)	Piperazine (15 wt%)
Solvent C	Water (70 wt%)	MDEA (25 wt%)	MEA (5 wt%)

4. ANALYTICAL METHOD DEVELOPEMENT

The tested methods were based on the literature survey (subtask 4) and the previous knowledge of amine and related compound analysis by Ramboll Analytics. When selecting proper analysis methods and materials for the tests some inconveniences were observed. For example, a sorbent material Ambersorb 572, widely used for nitrosamine extraction, was not available, since the production had been ended.

The method development was prioritized:

1. nitrosamines
2. alkylamines
3. solvent amines
4. aldehydes
5. ammonia
6. amides

The development of the analytical method was started with step by step method optimization, thus, at this point the methods for the analysis have been tested with standard substances and apply for pure water matrice only. However, some preliminary tests for test samples have also been performed. The testing has been done using chromatographic methods, in particular gas chromatography-mass spectrometry (GC-MS), gas chromatography-high resolution mass spectrometry (GC-HRMS) and ultra performance liquid chromatography (UPLC) coupled to tandem mass spectrometry (MS/MS). Also high performance liquid chromatography with reflactive index detector (HPLC-RI) or UV detector was tested for amide, aldehyde and ammonia analysis. After testing the suitability of the analytical devices, the pretreatment step with compound extraction and possible derivatization was under interest.

Keeping in mind the the practical issues during emission measurement, such as minimize number of parallel sampling lines, isokinetic sampling principle and maximize the sample gas volume to obtain lower detection limits the ideal goal was to have one rugged method for analysis of most of the componenents from the one sampling line. Based on this, the method development was started from the methods where derivatization was not utilized, excluding formaldehydea and acetaldehyde.

The term instrument detection limit (IDL), frequently used in the text, is the concentration of an analyte that is required to produce a signal greater than three times the standard deviation of the noise level (signals of the background). The method detection limit (MDL) includes all steps of the analysis instead.

The summaries of the tests performed are presented at the appendixes. Test sheets include description about the test, summary of the results and conclusions. The raw data is not presented.

4.1 Nitrosamines

The analytical method development was started with a quantitative method since it was assumed to be the most demanding but the screening and group methods will also be developed. For screening and group methods, method of lower sensitivity, such as colour reaction with nitroso group and analysis using spectrophotometric method or HPLC with ultraviolet/visible (UV/vis) detector, might be applicable. At this point for volatile nitrosamines GC-MS SCAN is recommended.

4.1.1 UPLC-MS/MS method optimization for pure substances

The development of the MS/MS method was the following. Multiple reaction monitoring (MRM) mode was selected to quarantee the selectivity and specificity. Each of the compounds was optimized for two daughter ions. Different eluents (H_2O/MeOH solutions) were tested as well as the effect of pH for maximizing the sensitivity.

The UPLC method development was started with testing of different columns for obtaining the optimum gradient method. The first column tested was Waters UPLC T3 (10 cm x 2.1 mm, 1.7 µm). The analysis was done without derivatization using H_2O and MeOH as eluents. Injection solvent was H_2O or 20% MeOH, since MeOH content above 20% was found to be not suitable for the

analysis (some of the studied compounds were not adsorbed on the column). Injection volume 5 µl was used.

When analyzing the test samples with direct injection, a significant matrice effect was noticed with the Waters UPLC T3 column (H_2O and MeOH as eluents). A more suitable column (lower matrice effect but longer analysis time) was found to be Discovery HS F5 (15 cm x 2.1 mm, 3 µm) from Supelco. Suitable eluents were 0.02% HCOOH and 0.02% HCOOH in acetonitrile. Injection solvent was H_2O and injection volume 5µl.

The IDL for nitrosopiperazine and NDELA was 1 µg/l and for NMOR, NPIP and 1,4-dinitrosopiperazine 5 – 15 µg/l. At the tests, NDEA and NDMA were optimized with MS/MS (poor sensitivity) but were not detected by any of the tested columns.

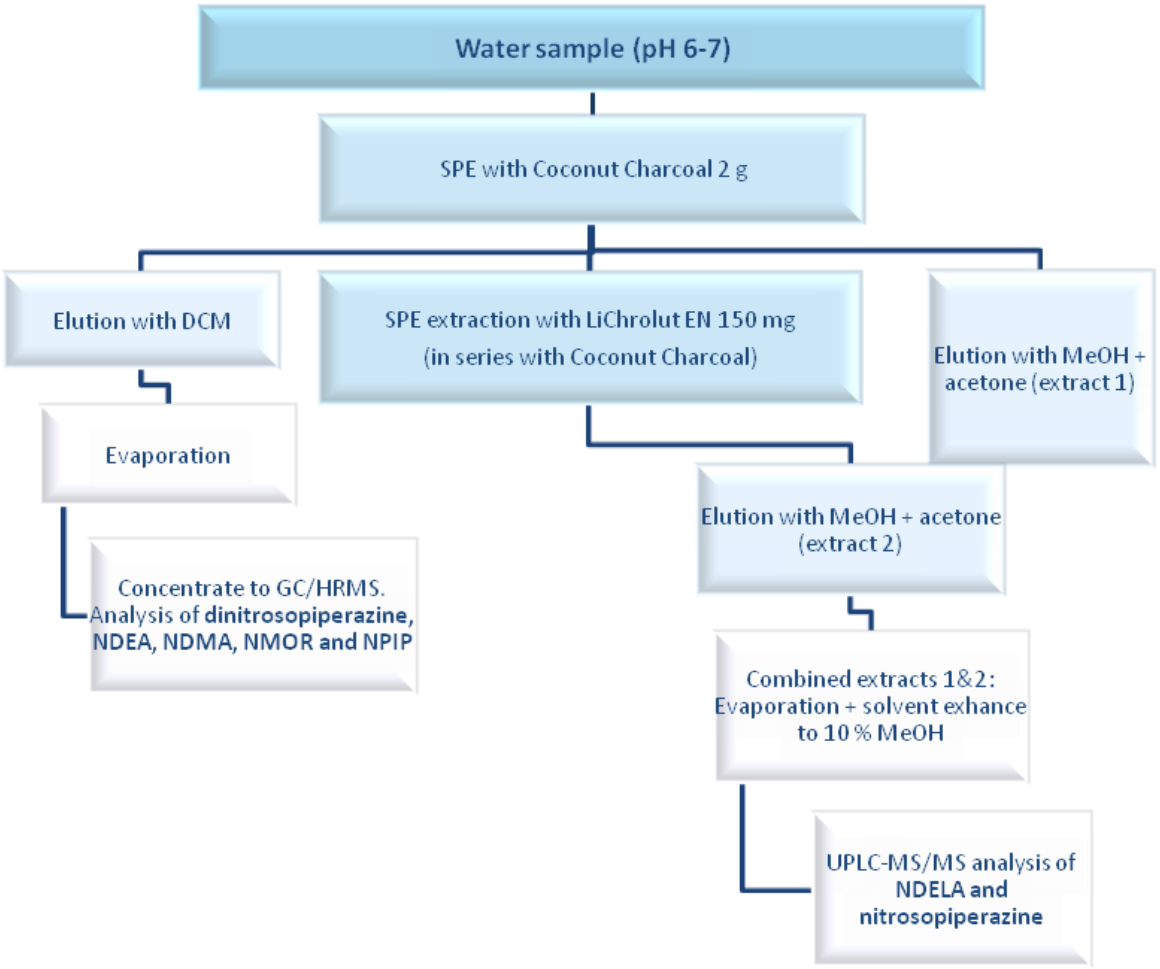
4.1.2 GC-HRMS method optimization for pure substances

The HRMS method was used with a single-ion monitoring (SIM) mode with the resolving power of 5 000. In the GC method splitless injection with a volume of 1 µl and the column Restek Rtx-5Sil MS (30 m x 0.25 mm, i.d. 1 µm) was used.

The IDL for volatile nitrosamines (1,4-dinitrosopiperazine, NDEA, NMOR, NPIP and NDMA) was mainly 1 – 10 µg/l or even less. However, in NDMA determination some tailing of the peak occurred. The IDLs were considerably higher for nitrosopiperazine and NDELA (200 – 1 000 µg/l). Similar derivatization as for primary and secondary alkylamines might be needed for nitrosopiperazine determination with GC. In case of NDELA the problem is assumed to occur from the two OH-groups of the molecule.

4.1.3 Concentration of nitrosamines, SPE extraction

The pretreatment of samples for nitrosamine analysis for GC and LC analyses was the following:



SPE cartridges are washed prior to use with hexane, dichloromethane, methanol and water in this order (the volume for LiChrolut EN 200 mg/6 ml, Merck is 3 ml of each and for Supelclean Coconut Charcoal 2g/6ml, Supelco the volume is 6 ml of each).

Water sample (pH 6-7) spiked with deuterated internal standards (NDMA D6, NMor D8 and NDELA D8) is passed though the SPE cartridges (Coconut and LiChrolut connected together so that the Coconut is on top and the sample hits it first) (the preconcentration step). After sample loading the sorbents are dryed with nitrogen for 60 min.

The Coconut sorbent is eluted with 2 x 6 ml of dichloromethane and the elute is passed through an 2,5 g Na_2SO_4 SPE cartridge (IST Isolute). The extract is concentrated to volume of 500 µl under stream of nitrogen. The analysis and quantification of dinitrosopiperazine, NDEA, NDMA, NMor and NPip are done by GC-HRMS using deuterated internal standards and external standard samples (standard compounds in the consentration range of 1-200 µg/l in the final injection solution to GC are spiked to deionized water) that are prepared the same way as samples. Blank sample (deionized water) and a sample matrix spiked with the analyzed compounds is also prepared the same way.

After dichloromethane the coconut sorbent is eluted with 6 ml of methanol and then with 6 ml of acetone (ectract 1 in the picture containing NDELA). The LiChrolut EN sorbent is eluted with 3 ml of methanol and then with 3 ml of acetone (ectract 2 in the picture containing nitrosopiperazine). Combined extract of 1 and 2 are evaporated with nitrogen to 1 ml and then 500 µl of deionized water is added to it. Evaporation is continued to the final volume of for example 500 µl and then 50 µl of methanol is added. The analysis and quantification of NDELA and nitrosopiperazine are done by UPLC-MS/MS using deuterated internal standards and external standard samples (standard compounds in the consentration range of 1-200 µg/l in the final injection solution to LC are spiked to deionized water) that are prepared the same way as samples. Blank sample (deionized water) and a sample matrix spiked with the analyzed compounds is also prepared the same way.

With deionized water as sample matrix up to 500 ml of sample volume can easily be used with the SPE cartridges. Deionized water added with 0.05, 0.5, 5 and 30 % of MEA was also tested with 10 and 100 ml of sample volume. The sample preparation was able to go through only with the 0.05 and 0.5 % of MEA content. 5 and 30 % of MEA was not ok. It seems that MEA is also at least partly retained by the SPE sorbent, this effect the sorbents capability to retain others and also the MEA is consentrated to the final ectract and it seems to interfere in the analysis.

Because the problems with 0.05 and 0.5% of MEA synthetic samples with nitrosoamines needs to be done again (nitrosopiperazine is not repeatable, the recovery is around 40% or nothing). Also some other than SPE concentration step will be considered. Also a method to remove the MEA before the consetration step is explored.

It should be noted that studies conducted by Padhye *et al.* 2010 showed that all tested active charcoals transformed secondary amines to N-nitrosamines at some extent. It was focused that about 90 % of transformation take plave on air drying step of SPE cartridge. This is important to take account on flue gas sampling step, where air and moisture are passing through the sampling medium e.g. charcoal to avoid false positives.

GC-HRMS analysis

The IDL for volatile nitrosamines (1,4-dinitrosopiperazine, NDEA, NMOR, NPIP and NDMA) was mainly 1 – 10 µg/l.

The HRMS method was used with a single-ion monitoring (SIM) mode with the resolving power of 5 000. In the GC method splitless injection with a volume of 1 µl and the column Restek Rtx-5Sil MS (30 m x 0.25 mm, i.d. 1 µm) was used.

LiChrolut EN (200 and 500 mg, Merck) and Coconut Charcoal (2 g, Sigma-Aldrich) were tested for extraction of nitrosamines from water. The recoveries for dinitrosopiperazine, NDEA and NMOR were high with LiChrolut EN but poor for the rest of the tested nitrosamines. However,

good recoveries were obtained with Coconut Charcoal for all the nitrosamines, except for NDELA and nitrosopiperazine. The GC-HRMS analysis was performed in dichloromethane (DCM) solution (used for elution). The recoveries were good for NDELA with Coconut Charcoal when the elution was done with MeOH and acetone after DCM (analysis with UPLC-MS/MS).

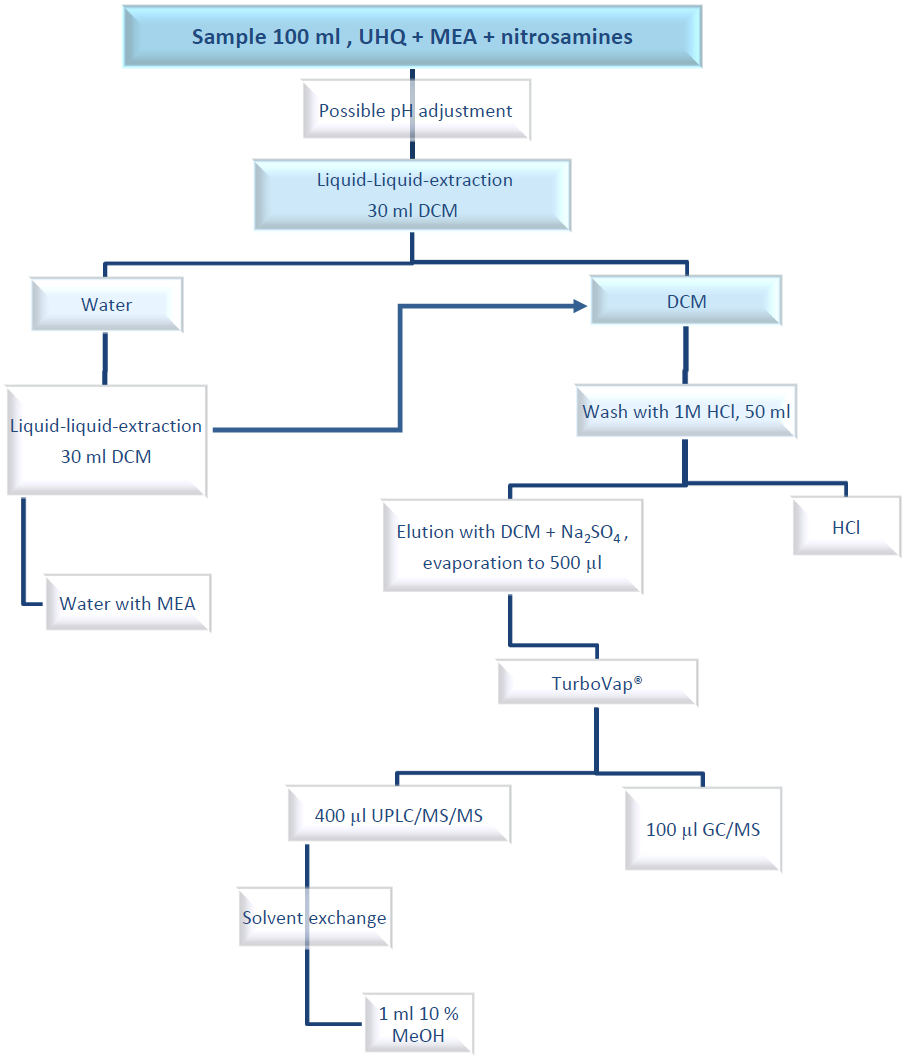
Since Coconut Charcoal was found to be the best sorbent material for the nitrosamines, it was selected for further testing. For nitrosopiperazine more SPE sorbent materials will be tested (analysis can be performed alternatively with direct injection to UPLC-MS/MS).

UPLC-MS/MS analysis
The UPLC-MS/MS istrumentation used consisted of Waters Acquity UPLC and Xevo TQ MS. A volume of 5 µl of sample was injected at the flow rate of 0,4 ml/min on to a Discovery HS F5 (15 cm x 2.1 mm, 3 µm) from Supelco. The column temperature was 40 ^{o}C. The capillary voltage was 3,6 kV, source temperature 150 ^{o}C and desolvation temperatue 600 ^{o}C. Cone gas flow 50 L/Hr, desolvation gas flow 1000 L/Hr and collosion gas flow 0,20 ml/min was used.

The mass spectrum was operated in MRM mode. The cone voltage and collision energy was optimized for each transition in positive ion mode. The IDL for nitrosopiperazine and NDELA was 1 µg/l and for NMOR, NPIP, and 1,4-dinitrosopiperazine 5 – 15 µg/l. With preconstration factor of 1000 the MDLs in a sample are ca. 0,005 µg/l for NDELA and nitrosopiperazine (including all the sample preparation steps, recovery from SPE etc.).

4.1.4 Nitrosamines, sample preparation and clean-up procedure by LLE

Because of the interferences caused by MEA in the previously mentioned SPE method an LLE procedure has been tested for synthetic water samples containing MEA. The yet to be optimized method is the following:



Synthetic sample for the extraction test was prepared by adding 100 ml of water into a separating funnel which has been previously washed with dichloromethane. Subsequently native standards and MEA were added to the funnel. Final concentration of MEA was from 0.5 % to 5 % and the concentration of nitrosamines has been 10 µg /L. Extraction step is done with dichloromethane for 4 minutes and the DCM phase is let to settle before the separation from the aqueous phase. The extraction step is repeated at least once. The combined DCM phase can still contain free amines which are removed with an additional clean-up step with 50 mL hydrochloric acid (1M) again for 4 minutes. After the acid wash the DCM phase is dried using sodium sulfate. Finally DCM phase is evaporated to 500 µL with a TurboVap® II concentration workstation.

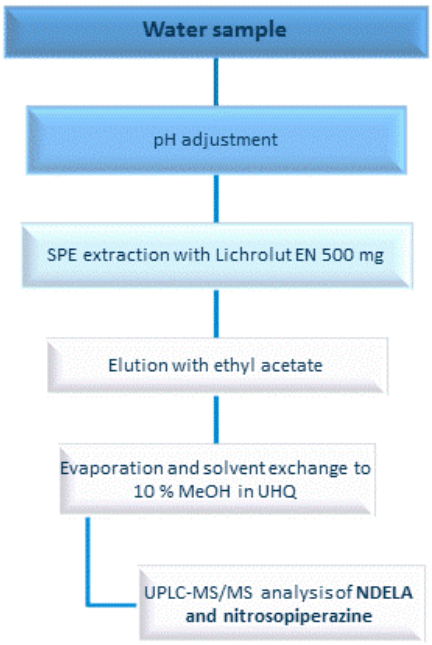
The concentrated sample is divided so that an aliquot of 100 µL is analysed directly by GC/MSD and for the remaining 400 µL of DCM a solvent exchange to 10 % MeOH in water is done. This part of the sample goes to the UPLC-MS/MS.

By this method results were promising for the "volatile nitrosamines" 1,4-dinitrosopiperazine, NDEA, NMOR, NPIP and NDMA with an initial recovery being over 50 % recardless of MEA concentration (0.5% - 5%).

Labeled standards are needed for the all compounds of interest to obtain reliable recovery and detection limits.

Because of the difficulties caused by high MEA concentrations sample preparation of nitrosamines was divided into two separate methods. 1,4-dinitrosopiperazine, NDEA, NMOR, NPIP and NDMA were concentrated using LLE as mentioned before. Recoveries of 50-75 % were achieved. Method was tested by synthetic samples volumes up to 100 mL. At the tested MEA concentrations the maximum estimated concentration factors can be from 500 to 750 (final volume of 100 µL). At this point where the GC-HRMS method was applied, the method detection limits for the 1,4-dinitrosopiperazine, NDEA, NMOR, NPIP and NDMA were about 2-20 ng/l for a single component (5 % MEA matrix). However lower detection limits are achieveable.

NDELA and N-nitrosopiperazine were extremely difficult to concentrate using LLE so these two compounds were concentrated with SPE. The method used was LiChrolut EN cartridge (6 mL/500 mg) and ethyl acetate as elution solvent. For NDELA recovery over 40 % and for N-nitrosopiperazine recovery over 30 % was achieved. However, because relatively low recovery percent, individual isotope labeled standards for both compounds should be used. Also the recoveries are very dependent on pH so an accurate pH adjustment is needed. The SPE method was following:



The detection limit of the NDELA from 5 % MEA matrix was at the point about 0,02 µg/l.

Validation of the LLE-method for nitrosamines was started with synthetic sample matrixes containing 5 vol-% MEA. Extractions in three replicates were done with dichloromethane in the range of 0.2 – 100 ng/L. Samples were analysed with GC/HRMS and the results showed that level of quantification for this type of matrix is 1 ng/L. However NDMA and N-nitrosomorpholine suffered from higher background when compared to other nitrosamines (NDEA, NPIP and 1.4-dinitropiperazine). The recoveries for NDMA proved to be lower than expected according to initial tests. Extraction parameters still need further work for optimizing the recoveries. Also HRMS parameters require some improvements (background issues with NDMA and NMOR).

The leftover waterphase from LLEs (500 mL) was pretreated according to planned concentration step for NDELA and N-nitrosopiperazine. This test was unsuccesful as neither one of the analytes could be detected. It is possible that the sample volume used was too large for LiChrolut EN cartridge. For now on a maximum of 100 mL should be used.

The artefact formation on acidic conditions is avoided at pH adjustment step. However the effect of pH adjustment is not validated.

4.1.5 Nitrosamine, further work and recommendations

Method validation should continue by optimization of concentration and pretreatment steps. Also parameters both UPLC-MS/MS and GC-HRMS should be enhanced. The validity and conservation of the sample should be evaluated based on studies with e.g. NOx.

4.2 Alkylamines

4.2.1 UPLC-MS/MS method optimization for pure substances

The development of the MS/MS method was the following. MRM mode was selected to quarantee the selectivity and specificity. Each of the compounds was optimized for two daughter ions excluding methylamine. Different eluents were tested as well as the effect of pH for maximizing the sensitivity.
When developing the method for UPLC, different columns and eluents were tested for finding the optimum gradient method. The selected column was Discovery HS F5. Suitable eluents were 0.02% HCOOH and 0.02% HCOOH in acetonitrile, injection solvent was H2O or MeOH and injection volume 5µl.
The IDL for alkylamines was found to be 10 µg/l.
No derivatization was performed but the extraction of the compounds was tested with six cation exchange columns: Oasis MCX (mixed mode cation exchange, 150 and 500 mg, Waters), Oasis WCX (mixed mode weak cation exchange, 150 mg, Waters) and Strata-X-C (phase similar to MCX, 500 mg, Phenomenex). For MCX and Strata-X-C the sorbent was washed after sample thoughput with 2% HCOOH and MeOH and the final elution was done using 5% NH4OH in MeOH. For WCX the sorbent was washed after sample throughput with 5% NH4OH and MeOH and the final elution was done with 2% HCOOH in MeOH. The analysis was performed from the eluate after consentration. Moderate to good recoveries of alkyl amines (except for MMA and TMA) were received with MCX columns and mainly poor with the rest (no peaks, except for TEA, were observed in the chromatogram when using Strata-XC column in extraction).
Basically, concentration method works for pure matrix if significant amount of solvent amines for all alkylamines except trimethylamine. However later it was observed that it could be concentrated by the purge and trap.

4.2.2 GC-MS method with benzoyl derivatization

Derivatization with benzoyl chloride and extraction by styrene-divinylbenzene (SDB) solid-phase extraction (SPE) columns (J.T.Baker) was tested, even though tertiary alkylamines were expected not to be derivatized (Rampfl et al. 2008). However, scan run from standard injection was poor and only few compounds could be determined from the spectrum.

4.2.3 Sample preparation by SPE

SPE cartridge (Oasis MCX 150 mg/6 ml, WatersE) was activated with 3 ml of methanol, and conditioned with 3 ml of water. Water sample (pH 3, adjusted with HCOOH) spiked with deuterated internal standards (diethylamine D10 and triethylamine D15) was passed though the SPE cartridge.
With deionized water as sample matrix up to 200 ml of sample volume can easily be used. Deionized water added with 0.05 and 0.5 of MEA was also tested with 10 and 100 ml of sample volume.
The sorbent was washed with 4 ml of 2% HCOOH and after that with 4 ml of methanol. The analytes were eluted from the sorbent with 2.5% NH_4OH in methanol. The extract was evaporated to the final volume for example 1 ml.

The UPLC-MS/MS istrumentation used consisted of Waters Acquity UPLC and Xevo TQ MS. A volume of 5 µl of sample was injected at the flow rate of 0.4 ml/min on to a Discovery HS F5 (15 cm x 2.1 mm, 3 µm) from Supelco. The column temperature was 40 ^{o}C. The capillary voltage was 0.5 kV, source temperature 150 ^{o}C and desolvation temperatue 600 ^{o}C. Cone gas flow 50 L/Hr, desolvation gas flow 1000 L/Hr and collosion gas flow 0.20 ml/min was used.

The mass spectrum was operated in MRM mode. The cone voltage and collision energy was optimized for each transition in positive ion mode. The IDL for alkylamines was found to be 10 µg/l. With preconstration factor of 200 the MDLs in a sample are around 0.05-0.1 µ/l for (including all the sample preparation steps, recovery from SPE etc.).

For alkylamines several SPE tests were done with different parameters. Results showed that only diethylamine and triethylamine could be concentrated reliably with SPE when synthetic sample contains MEA. From pure water all but trimethylamine can be concentrated with cation exchange cartridges.

4.2.4 Extraction of MEA using purge and trap

Because of the problems with SPE a new approach for separating and concentrating underivatized alkylamines was applied. The method-in-development is based on "purge and trap" –type of operation where the sample containing percentual amounts of MEA (pH >12.5) is purged with steady nitrogen flow. The sample is heated and sonicated and salts of sodium chloride and potassium sulphate are added to saturation point. The trap consists of two flasks containing 0,1 M hydrogen chloride which are connected in series and held in cooling bath. Method looks promising as trimethylamine could be separated almost completely from MEA solution with this method and if heat is added also other alkyalmines could be purged from sample solution. However due to technical difficulties and timelines reliable results are not available.

4.2.5 Sample preparation by SPE at pH 10.7

pKa of MEA is 9.5 and pKa's for alkylamines are:

Diethylamine (DEN)	11,02
Dimethylamine (DMA)	10,68
Ethylamine (EA)	10,7
Methylamine (MMA)	10,63
Triethylamine (TEA)	10,75
Trimethylamine (TMA)	9,8

There was a slight possibility to extract most of alkylmamines with better recovery than MEA. However empirical tests revealed that only triethylamine was obtained with reasonable recovery.

4.2.6 Sample preparation by ion pair exchange

LLE was tested by formation of an ion-pair with BEHPA (bis-2-ethylhexyl phosphate). Ion-pair reagent was diluted in chloroform. 2 % MEA solution was tested with spiked alkylamines. Experiment failed. The chloroform phase became very thick and oily, maybe because of MEA

4.2.7 Conclusions and further work

Alkylamines are still causing difficulties. Purge and trap method should be fully evaluated because if working, it may offer relatively powerful way for the concentration step further. If failed, it is possible that a derivatization step must be added for a succesful analysis.

Afternote: 1-Naphthyl isothiocyanate (NIT) based derivatization method was established after the publish of draft report of subtask 5. The method was promising for the the alkyl- and solventamines excluding MDEA, AMP, TEA, and TMA. Significant benefit was observed with piparzine (better response on UPLC-MS/MS) and MEA (also 2.nd transition was observed).

It appears that derivatisation is prefereable analysis if there is no need for the analysis of tertiary amines. If piperazine is important to analyse on very low concentrations, derivatization is preferable.

4.3 Solvent amines

4.3.1 UPLC-MS/MS method optimization for pure substances

The procedures for development of MS/MS and UPLC methods were the same as for alkylamines. Also the same columns, eluents and other conditions were used.

The IDL for solvent amines was found to be 5-10 µg/l, except for piperazine and EDA (IDLs 300 µg/l and 1 000 µg/l).

No derivatization was performed but the extraction was tested similarly to alkylamines with four cation exchange columns: Strata-X-C (500 mg), MCX (150 and 500 mg) and WCX (150 mg). MCX and Strata-X-C columns gave moderate to good recoveries (except for EDA and piperazine), while no peaks were observed in the sample extracted with WCX.

MCX column was selected for further tests since it was the most suitable for alkylamines, thus two of the compound groups can be analyzed with the same method.

4.3.2 GC-MS, method optimization for pure substances

The solvent amines were tested with alkylamines but the method was found to be not suitable since hardly any peaks were found from the spectrum.

4.3.3 Conclusions and further work

All solvent amines can be analyzed by direct injection to LC-MS/MS or by consentrating (not EDA and piperazine) by water sample with the MCX SPE cartridge.

4.4 Amides

4.4.1 UPLC-MS/MS, method optimization for pure substances

Amides were not detected without derivatization and thus can not be analyzed directly as for example alkylamines.

4.4.1 GC-MS, method optimization for pure substances

The amides were tested with alkylamines but the method was found to be not suitable since hardly any peaks were found from the spectrum.

4.4.2 HPLC-RI, method optimization for pure substances

Suitability of different analytical columns for amine analysis was examined when using HPLC-RI. Shodex RSpakDE-413 and Waters Bondapak C18 columns were tested. With RSpakDE-413 no peaks were detected and with Bondapak C18 a poor signal at the side of a solvent peak (water) was observed.

The analysis with HPLC-RI with the column Nucleosil 100-5 SA was tested 0.05 ml/l KH_2PO_4 at pH 2.6 as eluent with the flow rate of 1 ml/min. Acetamide and formamide are eluted right after the solvent signal so the retention is not good. Deionized water spiked with 100, 200 and 500 mg/l (injection volume 20 µl) are suitable but higher consentration are coeluted with the solvent.

Test samples id G 2009-11-06 and the solvent sample id P 2010-02-12 were analyzed (and diluted up to 1:40) and spiked with standard but matrix interferences were so high from the sample that these standard spikes were not detected.

4.4.3 Conclusions and further work

GC-MS methods with derivatization should be evaluated. Also HPLC eluents and conditions should be evaluated.

4.5 Aldehydes

Acetaldehyde was tested with the HPLC-RI with amides but acetamide and formamide are almost coeluted so this is was found to be not a working method.

Acetaldehyde was tested with headspace-GC-MS method (basic method in Ramboll Analytics). Synthetic test samples with MEA content of 0,5 and 30-40% was tested. MEA is interfering and therefore the MDL is around 5 mg/l with the MEA content of 0,5% and at 500 mg/l with the MEA of 30-40 %.

The headspace-GC-MS method was the following:

The Instrument used was TurboMatrix 40 Headspace sampler, Autosystem XL GC and TurboMass Gold MS from Perkin Elmer.

10 ml of water sample is bottled to the headspace sample vial and 1 g of NaCl is added. Standards with a known amount of acetaldehyde was prepared to deionized water. The water sample was heated for 30 min in 60 ^{o}C in an automated headspace sampler. The sample was pressurized with helium (22 psi for 0,5 min) and injected automatically (injection time 0,08 min) to GC. The carrier gas in GC was helium at the flow rate of 1,9 ml/min and the column was RTX-1701,1 µm, 60 m, i.d./o.d. 0.32/0.44 mm (Restek).

Method based on Journal of Chromatography A, 1216 (2009) 6554-6559 was established. Limit of detection for HPLC-UV was determined to be approximately 50µg/L (S/N=3) for both formaldehyde and acetaldehyde. The instrumental method was tested to be linear at range 0,1-10mg/l. The expected MEA (mono ethanolamine) concentration in the aqueous sample did not have an effect on this pre-treatment method. The spiked samples with and without MEA gave similar results. However pre-treated samples spiked with standard levels did not give linear results at the range 0,1-10 mg/L. This is hypothesized to be due to the cartridge capacity and/or the amount of derivatization solution. This issue remains to be tested.

4.5.1 Conclusions and further work

The method was found to be suitable for aqueous samples containing MEA. If the limit of detection needs to be lower, the method is easy to transfer to HPLC-MS. The issue of linearity of pre-treated standards can be solved with one or two simple tests. If this does not give acceptable results, also liquid-liquid extraction could be used.

4.6 Ammonia

Ammonia determination was tested as a benzoyl chloride derivative with alkyl amines by GC-MS, SIM-mode. The derivatization and analysis worked out and the method detection limit (MDL) was found to be around 1 mg/l. However, the method procedure is rather complicated and other methods for ammonia determination, such as distillation, spectrophotometric analysis or IC should be evaluated. Generally, the problems with widely used ammonia analyzing methods are the interferences with amine grop.

It seems that ammonia shall be analyzed separately from the other studied compounds. The amount of ammonia in the flue gas is expected to be considerably high (up to 50 ppmv) compared to the amines (<5 ppmv).

4.6.1 Conclusions and further work

Ammonia method for IC should be optimized (column, eluents and temperatures). For lower detection limits HPLC-MSMS should be tested.

5. PROCEDURES

Followed sub-chapters describe the best available methods for the analysis of target compounds developed in the project.

5.1 Nitrosamines, GC-method

5.1.1 Scope

The method is applicable for analysis of aqueous samples, samples collected on absorbtion media such as Thermosorb-N cartridges and amine based CCS-plant fluegas, washwater and absorption amine solutions. Method is applicable for the following nitrosamines:

Compound	CAS number	Formula
N-nitrosodimethylamine (NDMA)	62-75-9	$C_2H_6N_2O$
N-nitrosodiethylamine (NDEA)	55-18-5	$C_4H_{10}N_2O$
N-nitrosomorpholine (NMOR)	59-89-2	$C_4H_8N_2O_2$
N-nitrosopiperidine (NPIP)	100-75-4	$C_5H_{10}N_2O$
N,N-Dinitrosopiperazine (DNPIPA)	140-79-4	$C_4H_8N_4O_2$

The concentration of solvent amines in matrix is tested up to 10 %.

5.1.2 Principle

Sample –spiked with mass-labeled internal standards- is extracted with dichloromethane prior to analysis with GC-HRMS –apparatus. Thermosorb-N samples are desorbed with 75/25 (v/v) dichloromethane/methanol solution.

5.1.3 Interferences

High concentration of solvent amines may interfere with the pretreatment and/or chromatographic separation. Maximum recommended solvent amine concentration is 5-10 %, when sample volume is 500 mL and final volume of sample extract is 500 µl.

5.1.4 Reagents

- Dichloromethane (J.T. Baker (high purity) or equivalent)
- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- UHQ water (Millipore or equivalent)
- Anhydrous NaSO4 (J.T. Baker (high purity) or equivalent)
- Hydrochloric acid (J.T. Baker (high purity) or equivalent)

5.1.5 Standards

High purity standards shall be used, for example

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

5.1.5.1 Internal standards (ISTD)

High purity standards shall be used, for example

- N-nitrosodimethyl-d6-amine (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %
- N-nitrosomorpholine-d8 (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %

5.1.5.2Calibration references

Standard solutions will be done at 10 mg/L concentration in methanol. External standards are diluted to the range of 10-500 µg/L. Typical standards are as followed:

- Std 1 (10 µg/L)
- Std 2 (50 µg/L)
- Std 3 (100 µg/L)
- Std 4 (300 µg/L)
- Std 5 (500 µg/L)

5.1.6 Equipments and apparatus

5.1.6.1Equipments

- Pipettes
- Vials
- Standard laboratory glassware

5.1.6.2Apparatus

- GC with high resolution mass spectrometry detection
- TurboVap –automated evaporating apparatus

5.1.7 Sample storage

Sample will be kept refrigerated or in freeze until pretreatment and analysis. The sample will be analysed as soon as possible after arrival to the laboratory.

5.1.8 Procedure for the analysis

5.1.8.1Cleaning of equipments

Recommended washing temperature is 80 °C with proper detergent.

5.1.8.2Blank sample

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

5.1.8.3Quality control

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

5.1.8.4Pretreatment and cleaning

If the whole sample is planned to be analyzed the container must be weighed before and after extraction. Internal standards are added (10 µL of 10 mg/L) to the sample. When possible a spiked sample is done to the sample matrix. Otherwise spiked sample will be done to UHQ-water with similar solvent amine concentration with samples (synthetic matrix).
Samples (including standards and quality controls) are extracted twice with dichlolomethane using total of 50mL solvent. The combined extracts are washed-up of with 50 ml of 1M HCl- solution. The cleaned extracts are then dried with anhydrous $NaSO_4$ and evaporated by TurboVap to 0.5 mL. Finally the samples are transferred to GC vials and analyzed.
Thermosorb samples are desorbed with dichloromethane/methanol solution. Elute the sample by gently forcing the desorption solvent through the air sampler at approximately 0.5 mL/min. Collect the first 1-mL portion of solvent in the volumetric flask labeled "A" and the second 1-mL of eluent in the flask labeled "B".

The separate extracts are washed-up of with 0,1 M HCl-solution, transferred to GC vials (2 ml) and analyzed.

5.1.8.5Analysis
Analysis of samples is done with GC-HRMS system. Minimum resolution of mass spectrometry is 8000 (5% peak height). The monitored masses are:

Compound	m/z of analytes	m/z of perfluorokerosene reference peaks (lock mass)
N-nitrosodimethylamine (NDMA)	74.0480	92.9952
N-nitrosodimethylamine-d_6	80.0851	
N-nitrosodiethylamine (NDEA)	102.0793	99.9936
N-nitrosomorpholine (NMOR)	86.0606 (and/or 116.0586)	92.9952
N-nitrosomorpholine-d_8	94.1100	
N-nitrosopiperidine (NPIP)	114.0793	99.9936
1,4-Dinitrosopiperazine (DNPIPA)	84.0687 (and/or 114.0667)	92.9952

GC-system should offer baseline separation of all studied nitrosoamines. Conditions as followed have been tested:

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

5.1.9 Calculating results
Results are calculated with TargetLynx software using quantification method for nitrosoamines Final results will be given in units corresponding to concentration of sample.

5.1.10 Uncertainty

Recovery varies between batches and should be corrected by labeled internal standards.

5.2 Nitrosamines, LC-method

5.2.1 Scope

The method is applicable for analysis of water samples containing nitrosamines from amine based CCS-plant fluegas, and environmental samples whenever the concentrations of solvent amines are at the same range as analytes. Method is applicable for the following nitrosamines:

Compound	CAS number	Formula
N-nitrosopiperazine	5632-47-3	$C_4H_9N_3O$
N-nitrosodiethanolamine (NDELA)	1116-54-7	$C_4H_{10}N_2O_3$

5.2.2 Principle
Sample –spiked with mass-labeled internal standard- is concentrated with solid phase extraction (SPE) prior to analysis with UPLC-MS/MS -apparatus

5.2.3 Interferences

High concentration of solvent amines will interfere with the pretreatment thus reducing the recovery. pH-value has great impact on recovery. Maximum recommended sample volume is 100 mL.

5.2.4 Reagents

- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- Formic acid (J.T. Baker (98 %) or equivalent)
- Acetonitrile (BDH Prolabo (LC-MS grade) or equivalent)
- Hexane (J.T. Baker (95 %) or equivalent)
- Dichloromethane (J.T. Baker (high purity) or equivalent)
- Ethyl acetate (J.T. Baker (HPLC-grade) or equivalent)
- UHQ water (Millipore or equivalent)

5.2.5 Standards

- N-Nitrosopiperazine (Chiron AS), 8986.4-100 mg, purity 98 %
- N-Nitrosodiethanolamine (Chem Service, Inc.), purity 99,5 %

5.2.5.1 Internal standards (ISTD)

- N-nitrosodiethanolamine-D8 (C/D/N Isotopes Inc.), Purity 98 %, Deuteration degree 98 %

5.2.5.2 Calibration references

Work solutions for standards will be done at 10 mg/L concentration. External standards are diluted to the range of 10-500 µg/L. Typical standards are as followed:

- Std 1 (10 µg/L)
- Std 2 (50 µg/L)
- Std 3 (100 µg/L)
- Std 4 (300 µg/L)
- Std 5 (500 µg/L)

5.2.6 Equipments and apparatus

5.2.6.1 Equipments

- Pipettes
- Vials
- Test tubes
- Standard laboratory glassware
- LiChrolut EN 500 mg/6mL (Merck) (SPE)

5.2.6.2 Apparatus

- UPLC with MS/MS detector
- Vacuum manifold
- TurboVap –automated evaporating apparatus

5.2.7 Sample storage

Sample will be kept refrigerated until pretreatment and analysis. The sample will be analysed as soon as possible after arrival to the laboratory.

5.2.8 Procedure for the analysis

5.2.8.1 Cleaning of equipments

Standard laboratory cleanliness. Recommended washing temperature is 80 °C with proper detergent.

5.2.8.2 Blank sample

Blank sample will be treated and analysed exactly as and with the actual sample.

5.2.8.3 Quality control

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

5.2.8.4 Pretreatment

If the whole sample is planned to be analysed the container must be weighed before and after extraction. Internal standard is added (10 µL of 10 mg/L) to the sample and its pH is adjusted to 8,6. When possible a spiked sample is done to the sample matrix. Otherwise spiked sample will be done to UHQ-water with same amounts of solvent amines as in sample (synthetic matrix).

SPE cartridges used for the analysis are firstly cleaned and conditioned with consecutive solvent washes using hexane, dichloromethane, methanol and UHQ –water. After this the sample is slowly added to the cartridge with the help of vacuum. After addition of sample the cartridge is dried with gentle flow of N_2-gas. SPE cartridge is then eluted with ethyl acetate and evaporated to 500 µL with TurboVap and 900 µL of UHQ is added and evaporation is continued until ethyl acetate layer is gone. 100 µL of MeOH is added and the sample is transferred to an LC vial and analysed.

5.2.8.5 Cleaning

5.2.8.6 Analysis

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

- N-Nitrosopiperazine 116,0958 → 85,9167 and 116,0958 → 43,9245
- NDELA 135,0958 → 103,9812 and 135,0958 → 73,8634

UPLC conditions are as followed:

- Column Supelco Discovery® HS F5 (150 x 2,1 mm, 3 µm)
- Column temperature 40 ºC
- Eluents 0,02 % HCOOH in UHQ (A) and 0,02 % HCOOH in acetonitrile (B)
- Injection volume 5 µL
- Gradient 95/5 (A%/B%) for 5 min, 75/25 at 13 min, 60/40 at 23 min, 50/50 at 30 min, 10/90 at 31 min and 95/5 at 32 min. Total run time 33 min

5.2.9 Calculating results

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

5.3 Alkylamines, UPLC-method

5.3.1 Scope

The method is applicable for analysis of water samples containing alkylamines from amine based CCS-plant fluegas, and environmental samples whenever the concentrations of solvent amines are at the same range as analytes. Method is applicable for the following alkylamines:

Compound	CAS number	Formula
Diethylamine (DEN)	109-89-7	$C_4H_{11}N$
Dimethylamine (DMA)	124-40-3	C_2H_7N
Ethylamine (EA)	75-04-7	C_2H_7N
Methylamine (MMA)	74-89-5	CH_5N
Triethylamine (TEA)	121-44-8	$C_6H_{15}N$

5.3.2 Principle

Sample –spiked with mass-labeled internal standard- is concentrated with cation exchange -solid phase extraction (SPE) prior to analysis with UPLC-MS/MS -apparatus

5.3.3 Interferences

High concentration of solvent amines will interfere with the pretreatment thus reducing the recovery.

5.3.4 Reagents

- Methanol (Fisher Scientific (HPLC-grade) or equivalent)
- Formic acid (J.T. Baker (98 %) or equivalent)
- Acetonitrile (BDH Prolabo (LC-MS grade) or equivalent)
- UHQ water (Millipore or equivalent)
- Ammonia solution (Merck 5432 (25 %)

5.3.5 Standards

- Diethylamine (DEN), (Chem Service Inc.) O-2046, Purity 99,5 %
- Dimethylamine (DMA), (Acros Organics), 2M in methanol
- Ethylamine (EA), (Acros Organics), 2M in THF
- Methylamine (MMA), (AccuStandard Inc.) M-1666A-DI-R-ADD1, 2510 µg/mL (in water)
- Triethylamine (TEA), (Chem Service Inc.) O-297, Purity 99,5 %

5.3.5.1 Internal standards (ISTD)

- Diethylamine D10, (C/D/N Isotopes Inc.), D-2137, purity 98 %
- Triethylamine D15, (C/D/N Isotopes Inc.), D-1221, purity 98 %

5.3.5.2 Injection standards

None

5.3.5.3 Sampling standards

None

5.3.5.4 Calibration references

Work solutions for standards will be done at 10 mg/L concentration. External standards are diluted to the range of 10-500 µg/L. Typical standards are as followed:

- Std 1 (10 µg/L)
- Std 2 (50 µg/L)
- Std 3 (100 µg/L)
- Std 4 (300 µg/L)
- Std 5 (500 µg/L)

5.3.6 Equipments and apparatus

5.3.6.1 Equipments

- Pipettes
- Vials
- Test tubes
- Standard laboratory glassware
- Oasis® MCX 6 mL/150 mg (Waters)

5.3.6.2 Apparatus

- UPLC with MS/MS detector
- Vacuum manifold
- TurboVap –automated evaporating apparatus

5.3.7 Sample storage

Sample will be kept refrigerated until pretreatment and analysis. The sample will be analysed as soon as possible after arrival to the laboratory

5.3.8 Procedure for the analysis

5.3.8.1 Cleaning of equipments

Standard laboratory cleanliness. Recommended washing temperature is 80 °C with proper detergent.

5.3.8.2 Blank sample

Blank sample will be treated and analysed exactly as and with the actual sample.

5.3.8.3 Quality control

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

5.3.8.4 Pretreatment

If the whole sample is planned to be analysed the container must be weighed before and after extraction. Internal standard is added (10 µL of 10 mg/L) to the sample and its pH is adjusted to 3. When possible a spiked sample is done to the sample matrix. Otherwise spiked sample will be done to UHQ-water with same amounts of solvent amines as in sample (synthetic matrix).

SPE cartridges used for the analysis are firstly cleaned and conditioned with consecutive washes of methanol and UHQ –water. After this the sample is slowly added to the cartridge with the help of vacuum. After addition of sample the cartridge is washed with 2 % formic acid in methanol followed by methanol. After wash-steps the cartridge is dried with gentle flow of N_2-gas. SPE cartridges are then eluted with 2,5 % NH_4OH in methanol. The elute is evaporated with gentle flow of N_2 and UHQ-water is added so that the final composition of sample is 10% methanol and 90 % UHQ water.

5.3.8.5 Cleaning

As described above

5.3.8.6 Analysis

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

- Diethylamine (DEN): 74,16 → 45,92 and 74,16 → 28,881
- Dimethylamine (DMA): 46,16 → 45,92 and 46,16 → 29,933
- Ethylamine (EA): 46,16 → 28,889 and 46,16 → 26,843
- Methylamine (MMA): 32,032 → 31,900
- Triethylamine (TEA): 102,224 → 73,953 and 102,224 → 57,910
- Diethylamine D10: 84,196 → 51,938 and 84,196 → 33,919
- Triethylamine D15: 117,296 → 64,888 and 117,296 → 85,031

UPLC conditions are as followed:

- Column Supelco Discovery® HS F5 (150 x 2,1 mm, 3 µm)
- Column temperature 40 ºC
- Eluents 0,02 % HCOOH in UHQ (A) and 0,02 % HCOOH in acetonitrile (B)
- Injection volume 5 µL
- Gradient 95/5 (A%/B%) for 5 min, 75/25 at 13 min, 60/40 at 23 min, 50/50 at 30 min, 10/90 at 31 min and 95/5 at 32 min. Total run time 33 min

5.3.9 Calculating results

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

5.4 Solvent amines, UPLC-method

5.4.1 Scope

The method is applicable for analysis of water samples containing high concentrations of solvent amines from amine based CCS-plant fluegas, wash water, process waters and environmental samples. Method is applicable for the following solvent amines:

Compound	CAS number	Formula
2-amino-2-methyl-1-propanol (AMP)	124-68-5	$C_4H_{11}NO$
Diethanolamine (DEA)	111-42-2	$C_4H_{11}NO_2$
N-methyldiethanol-amine (MDEA)	105-59-9	$C_5H_{13}NO_2$
Monoethanolamine (MEA)	141-43-5	C_2H_7NO
Piperazine*	110-85-0	$C_4H_{10}N_2$

***Instrumental response for piperazine is poor when compared to other solvent amines**

5.4.2 Principle

Sample is diluted to acceptable level and analysed with UPLC-MS/MS apparatus (Direct injection)

5.4.3 Interferences

High concentration of solvent amines will contaminate the analyzing apparatus and therefore dilution factor of at least 1000 000 should be used for first the run.

5.4.4 Reagents

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

5.4.5 Standards

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

5.4.5.1 Internal standards (ISTD)

- Diethylamine D10, (C/D/N Isotopes Inc.), D-2137, purity 98 %
- Triethylamine D15, (C/D/N Isotopes Inc.), D-1221, purity 98 %

5.4.5.2 Calibration references

Work solutions for standards will be done at 10 mg/L concentration. External standards are diluted to the range of 10-500 µg/L. Typical standards are as followed:

- Std 1 (10 µg/L)
- Std 2 (50 µg/L)
- Std 3 (100 µg/L)
- Std 4 (300 µg/L)
- Std 5 (500 µg/L)

5.4.6 Equipments and apparatus

5.4.6.1 Equipments

- Pipettes
- Vials
- Test tubes
- Standard laboratory glassware

5.4.6.2 Apparatus

- UPLC with MS/MS detector

5.4.7 Sample storage

Sample will be kept refrigerated until pretreatment and analysis. The sample will be analysed as soon as possible after arrival to the laboratory

5.4.8 Procedure for the analysis

5.4.8.1 Cleaning of equipments

Standard laboratory cleanliness. Recommended washing temperature is 80 °C with proper detergent.

5.4.8.2 Blank sample

Blank sample will be treated and analysed exactly as and with the actual sample.

5.4.8.3 Quality control

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

5.4.8.4 Pretreatment

Samples are diluted with UHQ water using multiple dilution steps. Samples are thoroughly mixed with every dilution step. When possible a spiked sample is done to the sample matrix. Otherwise spiked sample will be done to UHQ-water with same amounts of solvent amines as in sample (synthetic matrix).

5.4.8.5 Cleaning

5.4.8.6 Analysis

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

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

UPLC conditions are as followed:

- Column Supelco Discovery® HS F5 (150 x 2,1 mm, 3 µm)
- Column temperature 40 ºC
- Eluents 0,02 % HCOOH in UHQ (A) and 0,02 % HCOOH in acetonitrile (B)
- Injection volume 5 µL
- Gradient 95/5 (A%/B%) for 5 min, 75/25 at 13 min, 60/40 at 23 min, 50/50 at 30 min, 10/90 at 31 min and 95/5 at 32 min. Total run time 33 min

5.4.9 Calculating results

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

5.5 Formaldehyde, HPLC-method

5.5.1 Scope

The method is applicable for analysis of aldehydes from amine based CCS-plant fluegas, washwater, process liquid and environmental samples. Method is applicable for the formaldehyde and other aldehydes.
Derivatization and analysis is selective with aldehyde-group and tested to be suitable for aqueous samples at the concentration up to 35 % MEA.
Method is tested to be linear at concentrations of 0.1-10 mg/l on HPLC-UV system.

5.5.2 Principle

Sample is derivatizated and concentrated onto DNPH-coated SPE cartridge. After elution with acetonitrile sample is analysed by HPLC-UV.

5.5.3 Interferences

Not known.

5.5.4 Reagents and standards

- LiChrolut EN 500 mg/6ml (Merck)
- Acetonitrile (J.T. Baker or equivalent)
- 2,4-dinitrophenylhydrazine ≥ 99% (Sigma-Aldrich No. 42210-100G-F)

5.5.5 Standards

Storage of standards in freezer.

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

5.5.6 Equipments and apparatus

5.5.6.1 Equipments

- Pipettes
- Vials
- Test tubes
- Standard laboratory glassware

5.5.6.2 Apparatus

- HPLC with UV-detector
- Column: Waters Ltd. µBONDAPAK C18 10µm 125Å 3,9×300mm

5.5.7 Sample storage

Samples should be stored at the freezer.

5.5.8 Procedure for the analysis

5.5.8.1 Cleaning of equipments

Recommended washing temperature at 80 °C with proper detergent.

5.5.8.2 Blank sample

Blank sample will be treated and analysed exactly as and with the actual sample.

5.5.8.3 Quality control

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

5.5.8.4 Pretreatment

Adjust pH of aqueous samples to 1.5 with 1M HCl.
Elute 5.0 ml of ACN and 10 ml of MQ-water through LiChrolut EN 500mg/6ml cartridge.
Elute 20 ml of 0.05 mg/ml DNPH-solution (derivatization solution) onto cartridge.
Add 50 ml of sample onto the cartridge.
Elute aldehyde derivatives with 7 ml of acetonitrile, send first 2 ml to waste.

5.5.8.5 Analysis

Analysis of samples is done with HPLC-UV system at wavelength 360 nm.

HPLC conditions are as followed:

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

5.5.9 Calculating of results

Results are calculated using peak areas.

6. SUMMARY OF TEST METHODS

Method detection limits at current state are as below.

Table 4 the results of the test samples

Compound	MDL, Wash water matrix (cMEA=5%)	MDL, Solvent matrix (cMEA=35%)	Observations
Nitrosamines:			
1,4-dinitrosopiperazine**	0.1 ng/l	1 ng/l	
NDELA*	50 ng/l	350 ng/l	
NDEA**	0.1 ng/l	1 ng/l	
NDMA**	1 ng/l	10 ng/l	
NMOR**	1 ng/l	10 ng/l	
Nitrosopiperazine*	80 ng/l	600 ng/l	Variation on recovery
NPIP**	0.1 ng/l	1 ng/l	
Alkylamines:			
DEN	200 ng/l	1400 ng/l	
DMA	50 000 ng/l	350 000 ng/l	
EA	50 000 ng/l	350 000 ng/l	
MMA	100 000 ng/l	700 000 ng/l	Only one MRM-transition
TEA	200 ng/l	1400 ng/l	
TMA	1 000 ng/l	7 000 ng/l	
Solvent amines*:**			
AMP	0.05 mg/l	5.0 mg/l	
DEA	0.05 mg/l	5.0 mg/l	
EDA	10 mg/l	1.0 mg/l	
MDEA	0.01 mg/l	1.0 mg/l	
MEA	0.05 mg/l	5.0 mg/l	Only one MRM-transition
Piperazine	3.0 mg/l	300 mg/l	poor peak
Aldehydes			
formaldehyde	50 ug/l	50 ug/l	
acetaldehyde	50 ug/l	50 ug/l	
Amides			
formamide	n.d.	n.d.	
acetamide	n.d.	n.d.	
Ammonia			
GC-MS	about 1 mg/l	about 1 mg/l	
IC	under evaluation	under evaluation	

**UPLC-MS/MS*

***GC-HRMS*

****without concentration.*

7. ANALYSIS OF TEST SAMPLES

The wash water (expected MEA 0.5% = 5 000 mg/l) and amine solvent (expected MEA 30 – 40% = 300 000 – 400 000 mg/l) test samples delivered by the Company were analyzed with direct water injection after filtration and dilution by using UPLC-MS/MS. The high MEA content prevents the sample concentration and sample dilution needs to be done instead.

In addition to the direct injection, nitrosamines will be analyzed after SPE pretreatment with GC-HRMS, since NDMA and NDEA were not detectable with UPLC-MS/MS (SPE treatment needs some testing prior to analysis). It should be noted that the MDL is dependent of the dilution and the recovery-% of the standard addition.

Analyzed wash water sample was with id G 2009-11-06 and the solvent sample id P 2010-02-12.

The results for nitrosamines, alkylamines and solvent amines (with MDLs) from wash water and amine solvent sample, when analyzed with direct injection, are presented at Table 5. Analysis method for EDA and piperazine is semiquantitative.

Table 5 the results of the test samples

Compound	MDL mg/l, Wash water sample	Result mg/l, Wash water sample	MDL mg/l, Solvent sample	Result mg/l, Solvent sample
Nitrosamines:				
1,4-dinitrosopiperazine	0.20	n.d.	20	n.d.
NDELA	0.01	<0.01	1.0	n.d.
NDEA	n.a.	n.a.	n.a.	n.a.
NDMA	n.a.	n.a.	n.a.	n.a.
NMOR	0.20	n.d.	20	n.d.
Nitrosopiperazine	0.01	n.d.	1.0	n.d.
NPIP	0.15	n.d.	15	n.d.
Alkylamines*:				
DEN	0.05	n.d.	5.0	n.d.
DMA	0.05	n.d.	5.0	n.d.
EA	0.05	n.d.	5.0	n.d.
MMA	0.10	n.d.	50	n.d.
TEA	0.05	n.d.	5.0	n.d.
TMA	0.05	n.d.	5.0	n.d.
Solvent amines*:				
AMP	0.05	n.d.	5.0	n.d.
DEA	0.05	1.2	5.0	11
EDA	10	n.d.	1.0	n.d.
MDEA	0.01	n.d.	1.0	n.d.
MEA	0.05	3 500	5.0	380 000
Piperazine	3.0	n.d.	300	n.d.

n.a. = not available, n.d. = not detected
**direct injection after filtration and dilution to 10x, 100x and 1000 x.*

Nitrosamines were analyzed with Waters UPLC T3 and Discovery HS F5 columns. Waters UPLC T3 and the eluents used with the column were found to have noticeable matrice effect affecting to the sensitivity and thus are not suitable for direct injection. In addition, since the Discovery HS F5 column gave better signals after SPE pretreatment, the column was selected for the further testing.

8. CONCLUSIONS AND FURTHER WORK

The scope of this task was to test and finally create analytical methods for solvent amines and their degradation products possibly present in CO_2-capture unit. The work is based on the literature survey of sub-task 4 and the background knowledge of the amine analysis by Ramboll Analytics. N-nitrosamines and LMW alkylamines were the main focus of this task. Analytical methods for solvent amines, LMW amides, aldehydes and ammonia were also to be researched. The matrices of interest were the treated flue gas from the absorber column, the wash water from the absorber top and the rich and lean aqueous amine solution circulating in the absorber.

The work has been done with water matrice using pure standard substances and with syntetic wash water containing 5 % of MEA. Analysis has been done using chromatographic methods, in particular HPLC-RI, GC-MSd, GC-HRMS, UPLC-MS/MS and IC.

Two separate methods were established for the **nitrosoamine** analysis. First employes liquid-liquid extraction combined with GC-MS analysis and is suitable for NDMA, NDEA, NMOR, NPIP and 1,4-dinitrosopiperazine. Detection limit at this point was about 1 ng/l from wash water and 10 ng/l solvent amines, however, lower detection limits are practicable. For the NDELA, detection limit from 5 % MEA matrix was about 50 ng/l (about 350 ng/l for solvent amine) utilizing UPLC-MS/MS technique. Suitabale screening method for volatile nitrosamines is GC-MS at SCAN mode.

For the **solvent amines** analysis direct injection to UPLC-MS/MS or after dilution. The instrument detection limits (IDL) for solvent amines was found to be 5-10 µg/l, except for piperazine and EDA (IDL's 300 µg/l and 1 000 µg/l). The concentration step is possible but not evaluated detailed at this work, because expected relatively high concentration of solvent amines. In the future if lower detection limits are needed the SPE concentration should be tested.

From blank water matrix IDL for the **alkylamines** was found to be 10 µg/l. With preconsentration factor of 200 the MDLs in a sample is around 0.05-0.1 µg/l. The difficulties were observed when concentration step was employed with the sample including five percent of solvent amine. Different concentration methods were tested, such as SPE, LLE, purge and trap and ion pair without success. However, there was some good signs on purge and trap tests. Alkylamines were analysed by UPLC-MS/MS. Purge and trap test should be tested further with higher MEA concentrations. Effect of temperature and ultrasound should be evaluated as well as different conditions. If not working derivatization based methods should be established. Derivatization combined with purge and trap may be useful approach.

For **Formaldehyde and acetaldehyde** analysis DNPH derivatization was used. It was proved to be selective only for aldehydes and insensitive for amine concentration involved in matrix. Detection limit at this point was reached to 50 µg/l both washwater and solvent amines. If lower detection limits are needed, LLE concentration steps may be involved.

Also HS-GC-MSD method for acetaldehyde and heavier aldehydes were tested, but further tests were not performed due to lack of need and relatively high interference with solvent amines.

Ammonia analysis were tested with IC and derivatization followed by GC-MS analysis. IC tests were not fully evaluated within this time frame. However it works with blank water while high concentration of solvent amines causes co-elution and merged peaks related.

Ammonia was also analysed by derivatization and analysis by GC-MS. Method is also suitable for solvent amine concentrated samples. Detection limit at this point was about 1 mg/l. Lower detection limits may be obtained after detailed method development.

In future IC method should be developed further to reduce interference with solvent amines.

Tests for **Amides** were performed by GC-MS, UPLC-MS/MS and HPLC-RI. Only HPLC-RI gave response for the target amides in a blank water matrix. When MEA was involved as a solvent amine, no amides were observed. Derivatization methods for amides should be evaluated.

Further work to optimize methods, acquire lower detection limits and perform large validation is recommended. Also tests for the sorbent materials used at emission measurement and referred at the subtask 2 should be established. It is very important to take account the effect of relatively high concentration of solvent amines during the testing because as it was observerd with SPE-tests, it may reduce significantly retention volume of the absorbent. Also tests should include the impact of flue gas components and degradation.

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Liitteet

Test 1: Retention time on UPLC-MSMS, solvent and alkylamines, temp 20 °C

Scope:	UPLC-MSMS retention times, solvent and alkylamines
Description:	
Standard solution of 1000 µg/l in MeOH was analysed by UPLC-MSMS using HSFS5 column at temperature of 20 °C. MS mode was ES+ and m/z: TIC.	
Results:	

Compound	**RTT**
Diethylamine (DEN)	5.63
Monoethanolamine (MEA)	2.82
1,2-Diaminoethane (EDA)	20.3 (poor peak)
Trimethylamine (TMA)	3.79
Dimethylamine (DMA)	3.25
Ethylamine (EA)	3.33
Methylamine (MMA)	2.88
N-Methyldiethanolamine (MDEA)	3.35
Diethanolamine (DEA)	3.07
Triethylamine (TEA)	11.35
2-Amino-2-methyl-1-propanol (AMP)	4.12
Piperazine	22.21 (poor peak)

Conclusions:	
Most of the peaks RTT's within 3-4 min. Poor solvent composition for the analytes at the vial.	

Test 2: Retention time on UPLC-MSMS, solvent and alkylamines, temp 40 °C

Scope:	UPLC-MSMS retention times, solvent and alkylamines
Description:	

Standard solution of 1000 µg/l in MeOH was analysed by UPLC-MSMS using HSFS5 column at temperature of 40 °C. MS mode was ES+ and m/z: TIC.

Results:

Compound	**RTT**
Diethylamine (DEN)	5.76
Monoethanolamine (MEA)	2.89
1,2-Diaminoethane (EDA)	25.3 (poor peak)
Trimethylamine (TMA)	3.86
Dimethylamine (DMA)	3.33
Ethylamine (EA)	3.43
Methylamine (MMA)	2.96
N-Methyldiethanolamine (MDEA)	3.40
Diethanolamine (DEA)	3.14
Triethylamine (TEA)	11.49
2-Amino-2-methyl-1-propanol (AMP)	4.20
Piperazine	27.57 (poor peak)

Conclusions:

Most of the peaks RTT within about 3-4 min. No significant effect on peak shapes between temperatures of 20 °C and 40 °C.
Most of the peaks RTT's within 3-4 min. Poor solvent composition for the analytes at the vial.

Test 3: Alkyl- & solvent amine, formamide, acetamide, ammonia; benzoyl derivatization

Scope:	Derivatization of selected amines
Description:	

Based on method presented Analyst, 2001 126, p. 1663-1668.

1. SPE cartridge SDB 200mg/6ml (JT Baker) was activated by 1.3 ml of MeOH and purified by 3 ml of H2O.
2. Add 1 ml of 10 mg/l std-solution
3. Add 2 g NaHCO3
4. add 600 µl benzoyl chloride, shake 15 min
5. sample absorption into SPE cartridge (200 ml), wash 2 x 5 ml water
6. drying of SPE 30 min (nitrogen)
7. elution with 4 ml ethylacetate
8. evaporation -> 1 ml

Ammonia was also tested with two additional concentrations: 10 mg/l, 20 mg/l and later 50 mg/l.

Analysis by GC-MSD at SCAN-mode, HS5MS 30, 0,25 µm, 0,25 mm column

Results:
Dirty backgrounds. Large peak of benzoic acid. Only some of the compouds detected.

Conclusions:
Possible start point method for ammonia.

Test 4: Cation exchance SPE, solvent and alkylamines, blank water matrix

Scope:	Concentration of solvent and alkyamines by cation exchange cartridges (MCX 500 mg, MCX 150 mg, WCX and Strata)
Description:	

MCX and Strata

1. Test solution 100 µl of 10/mg/l added to 200 ml of distilled water.
2. pH adjusted to 3 by adding 50 µl HCOOH
3. Wash of MCX and Strata 4 ml formic acid
4. Sample extraction into the cartridge
5. 1. elution on 4 ml of 100 % MEOH
6. 2. elution on 4 ml 5 % NH4OH in MeOH

WCX

1. Wash of WCX 4 ml NH_4OH
2. Sample extraction into the cartridge
3. 1. elution on 4 ml of 100 % MEOH
4. 2. elution on 4 ml 5 % formic acid in MeOH

Analysis by UPLC-MSMS using HSFS5 column, eluents: A= 0,01 % HCOOH, B= 0,02 % HCOOH/ACN. Inj volume 5 µl.

Results:

Recoveries %	**Strata**	**MCX 500 mg**	**MCX 150 mg**	**WCX**
Methylamine (MMA)	7,8	64,9	22,1	0,1
Dimethylamine (DMA)	3,8	34,7	49,9	n.d.
Trimethylamine (TMA)	0,4	0,3	0,1	0,1
Ethylamine (EA)	7,8	40,8	57,4	n.d.
Diethylamine (DEN)	1,8	24,8	73,6	0,4
Triethylamine (TEA)	50,3	48,2	38,5	1,0
Monoethanolamine (MEA)	58,4	55,9	19,6	n.d.
Diethanolamine (DEA)	92,8	84,5	52,8	n.d.
N-Methyldiethanolamine (MDEA)	104,2	76,7	66,8	n.d.
2-Amino-2-methyl-1-propanol (AMP)	96,4	94,2	91,0	n.d.
1,2-Diaminoethane (EDA)	0	29,2	(543)	n.d.
Piperazine	(321,2)	(258,5)	(369)	n.d.

Conclusions:

500 mg MCX was best for methylamine while others were better on 150 mg MCX -> eluation volume should be increased respectively.

Use higer volume (12 ml) for second elution of 500 MCX. EDA is detected only on MCX 500 mg. In future MeOH exchange to water is not necessary.

WCX was not suitabale. Was neutralization correctly done?

Test 5: Cation exchance SPE (MCX), solvent and alkylamines, blank water matrix

Scope:	Concentration of solvent and alkyamines by cation exchange cartridges (MCX 500 mg, MCX 150 mg)
Description:	

MCX and Strata

1. Std. at 200 ml MQ-water
2. pH to 3
3. SPE: wash 3 ml MeOH followed by 3 ml water
4. Sample wash 2 % HCOOH
5. Sample wash 2 % MeOH
6. elution MCX 500 mg: 12 ml 5 % NH4OH/MeOH
7. elution MCX 150 mg: 4 ml 5 % NH4OH/MeOH
8. evaporation to 1 ml

Analysis by UPLC-MSMS using HSFS5 column, eluents: A= 0,01 % HCOOH, B= 0,02 % HCOOH/ACN. Inj. volume 5 µl.

Results:

Recoveries %	**MCX 500 mg**	**MCX 500 mg, no MeOH wash**	**MCX 150 mg**	**MCX 150 mg, no MeOH wash**
Methylamine (MMA)	187,9	0,8	28,0	0,4
Dimethylamine (DMA)	53,0		50,0	1,9
Trimethylamine (TMA)	0,6	5,3	0,9	
Ethylamine (EA)	37,6	0,6	66,0	0,9
Diethylamine (DEN)	79,1	114,2	79,4	120,8
Triethylamine (TEA)	49,1	87,1	46,9	88,5
Monoethanolamine (MEA)	20,7		23,2	
Diethanolamine (DEA)	22,2		55,7	20,0
N-Methyldiethanolamine (MDEA)	92,6		90,9	
2-Amino-2-methyl-1-propanol (AMP)	77,6	63,0	103,2	98,2
1,2-Diaminoethane (EDA)	0,7	1,2		1,0
Piperazine	21,0	9,3	9,3	9,3

Conclusions:

TMA recoveries better without MeOH wash, others worse or no recovery. Without MeOH significant noise on the baseline at the beginning of the run to all m/z.

EDA 1000 µg/l only direct standards detected, lower standards not. EDA and piperazine signals vanished at the end of the sample run (23. and 24. sample on the rack). New run revealed that it wasn't due to handling of the samples.

Problems with the MCX blank samples. With MMA small standard addition smaller than 1000 µg/l is not detected. Blanks need to be cleaned or direct injection.

Best results on MCX 150 mg with MeOH wash so far.

Test 6: MCX, 2,5 % ammonia elution test

Scope:	Concentration of solvent and alkyamines by cation exchange cartridges MCX 150 mg
Description:	

MCX and Strata

1. Std. at 200 ml MQ-water
2. pH to 3
3. SPE: was 3 ml MeOH -> 3 ml water
4. Sample wash 2 % HCOOH
5. Sample wash
6. elution MCX 150 mg: 4 ml 2,5 % NH4OH/MeOH
7. evaporation to 1 ml

Analysis by UPLC-MSMS using HSFS5 column, eluents: A= 0,01 % HCOOH, B= 0,02 % HCOOH/ACN. Inj. volume 5 µl.

Results:

Recoveries %	**MCX 150 mg**
Methylamine (MMA)	11,8
Dimethylamine (DMA)	39,0
Trimethylamine (TMA)	n.d.
Ethylamine (EA)	52,6
Diethylamine (DEN)	66,3
Triethylamine (TEA)	51,0
Monoethanolamine (MEA)	4,7
Diethanolamine (DEA)	40,5
N-Methyldiethanolamine (MDEA)	71,3
2-Amino-2-methyl-1-propanol (AMP)	88,3
1,2-Diaminoethane (EDA)	n.d.
Piperazine	n.d.

Conclusions:

Recoveries lower than on 5 % NH4OH/MeOH.

Test 7: LiChrolut SPE test for nitrosamines, GC-HRMS, blank water matrix

Scope:	LiChrolut SPE test for nitrosamines, GC-HRMS
Description:	200 mg/6 ml and 500 mg/6 ml LiChrolut were utilized for nitrosamine concentration. Analysis by GC-HRMS.

1. Added 1 g $NaHCO_3$ into 500 ml synthetic water sample (pH needs to be 6-8.5) pH 8. (7.4 best ?)
2. SPE clean-up and activation (500 mg LiChrolut on parentheses):

   200 mg LiChrolut
   5 ml hexane (8 ml)
   5 ml DCM (8 ml)
   5 ml MeOH (8 ml)
   5 ml H_2O (8 ml)

3. Extraction into SPE about 5 ml/min
4. Washup 5 ml H2O (10 ml)
5. elution 5 ml DCM (10ml)
6. evaporation to 1 ml (bath temperatures up to 40 °C has been used)
7. 100 µl injection into GC

GC-HRMS column RTx-5silMS, 30 m, id 0,2 mm, phase 1 µm.

Results:

Compound						
GC-HRMS	blank 200 mg Li-Chr.	200 mg Li-Chr. 100 µg/l concentration	200 mg Li-Chr. 200 µg/l concentration	blank 500 mg LiChr.	500 mg LiChr. 100 µg/l concentration	500 mg Li-Chr. 200 µg/l concentration
1,4-dinitrosopiperazine						
NDELA						
NDEA	0,0	171,4 %	119,7 %	0,0 %	163,9 %	152,0 %
NDMA	0,0	11,5 %	6,4 %	0,0 %	27,1 %	17,4 %
NMOR	0,0	139,8 %	71,1 %	0,0 %	172,6 %	130,0 %
Nitrosopiperazine	0,0	157,6 %	107,1 %	0,0 %	173,9 %	150,2 %
NPIP						

Conclusions:

No recoveries on 1,4-dinitrosopiperazine, NDELA and NPIP.

Test 8: LiChrolut SPE test for nitrosamines, UPLC-MSMS, blank water matrix

Scope:	LiChrolut SPE concentration test for nitrosamines, UPLC-MSMS, blank water matrix
Description:	200 mg/6 ml and 500 mg/6 ml LiChrolut were utilized for nitrosamine concentration. Analysis by UPLC-MSMS.

1. Added 1 g $NaHCO_3$ into 500 ml synthetic water sample (pH needs to be 6-8.5) pH 8. (7.4 best ?)
2. SPE clean-up and activation (500 mg LiChrolut on parentheses):

   200 mg LiChrolut
   5 ml hexane (8 ml)
   5 ml DCM (8 ml)
   5 ml MeOH (8 ml)
   5 ml H_2O (8 ml)

3. Extraction into SPE about 5 ml/min
4. Washup 5 ml H2O (10 ml)
5. elution 5 ml DCM (10ml)
6. evaporation to 1 ml (bath temperatures up to 40 °C has been used)
7. addition of 900 µl H2O and evaporation of DCM

Column, T3 2.1x100um; A= H2O, B =MeOH

Results:

Compound					
UPLC-MSMS	5. Lichrolut 200 mg/6ml, test c= 100 µg/l	6. Lichrolut 200 mg/6ml, test c= 200 µg/l	7. Lichrolut 500 mg/6ml, test c= 100 µg/l	8. Lichrolut 500 mg/6ml, test c= 100 µg/l	9. Lichrolut 500 mg/6ml, test c= 200 µg/l
1,4-dinitrosopiperazine	43.8 %	164.8 %	119.3 %	119.3 %	14.7 %
NDELA	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %
NDEA	87.3 %	58.5 %	94.3 %	94.3 %	67.4 %
NDMA	0.0 %	(550.3 %)	0.0 %	0.0 %	0.0 %
NMOR	37.7 %	38.3 %	68.7 %	68.7 %	57.0 %
Nitrosopiperazine	0.0 %	0.9 %	0.0 %	0.0 %	0.0 %
NPIP	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %

Conclusions:

Blanks ok. No recovery on NDELA, NDMA, nitrosopiperazine and NPIP.

Test 9: Coconut charcoal concentration for nitrosamines, GC-HRMS, blank water matrix

Scope:	Coconut charcoal SPE test for nitrosamines, GC-HRMS
Description:	2g/6 ml coconut charcoal was utilized for nitrosamine concentration. Analysis by GC-HRMS.

1. SPE clean-up and activation

   10 ml DCM
   10 ml MeOH
   10 ml H_2O

2. extraction into SPE. Sample amount 500 ml
3. drying 60 min on nitrogen (unnecessary step, see 5!)
4. elution 2x 6 ml DCM (10ml)
5. drying through 2,5 g Na2SO4 folowed by 3 ml DCM
6. evaporation by TurboVap to 0,5 ml temp. 20-25 °C
7. to GC-MS 100 µl injection

HRMS column RTx-5silMS, 30 m, id 0,25 mm, phase 1 µm. MS resolution 5000, tuning m/z 99.9936.
Oven program: 5min@35°C; 5°C/min to 180 °C (0 min); 30°C/min to 300°C (3 min)

Results:

Compound			
GC-HRMS	blank	2. Charcoal, test concentration 100 µg/l	3. Charcoal, test concentration 200 µg/l
1,4-dinitrosopiperazine	n.d.	n.d.	n.d.
NDELA	n.d.	n.d.	n.d.
NDEA	0,0	118,4	133,8
NDMA	0,0	88,2	113,1
NMOR	0,0	161,0	152,0
Nitrosopiperazine	0,0	146,8	130,7
NPIP	n.d.	n.d.	n.d.

Conclusions:

NPIP, NDELA and 1,4-dinitrosopiperazine: no recoveries.

Test 10: Coconut charcoal concentration for nitrosamines, UPLC-MSMS, blank water matrix

Scope:	Coconut charcoal SPE test for nitrosamines, UPLC-MSMS
Description:	2g/6 ml coconut charcoal was utilized for nitrosamine concentration. Analysis by GC-HRMS.

1. SPE clean-up and activation

   10 ml DCM
   10 ml MeOH
   10 ml H_2O

2. extraction into SPE. Sample amount 500 ml
3. drying 60 min on nitrogen (unnecessary step, see 5!)
4. elution 2x 6 ml DCM (10ml)
5. drying through 2,5 g Na2SO4 folowed by 3 ml DCM
6. evaporation by TurboVap to 0,5 ml temp. 20-25 °C
7. addition of 900 µl H2O and evaporation of DCM

Column, T3 2.1x100um; A= H2O, B =MeOH

Results:

Compound		
UPLC-MSMS	Coconut charcoal 2g/6ml Test concentration of 100 µg/l	Coconut Charcoal Test concentration of 200 µg/l
1,4-dinitrosopiperazine	20.6 %	21.9 %
NDELA	0.0	0.0 %
NDEA	23.3 %	46.3 %
NDMA	0.0 %	126.7 %
NMOR	46.8 %	40.9 %
Nitrosopiperazine	0.0 %	0.0 %
NPIP	0.0 %	0.0 %

Conclusions:

No recoveries on NDELA, nitrosopiperazine, NPIP.

Test 11: Nitrosoamines, SPE extraction test Coconut charcoal

Scope:	Nitrosoamines, SPE extraction test with coconut charcoal
Description:	2g/6 ml coconut charcoal was utilized for nitrosamine concentration. Analysis by GC-HRMS.

1. SPE clean-up and activation

   10 ml DCM
   10 ml MeOH
   10 ml H_2O

2. extraction into SPE. Sample amount 500 ml
3. drying 60 min on nitrogen (unnecessary step, see 5!)
4. elution 2x 6 ml DCM (10ml)
5. drying through 2,5 g Na2SO4 folowed by 3 ml DCM
6. evaporation by TurboVap to 0,5 ml temp. 20-25 °C
7. addition of 900 µl H2O and evaporation of DCM

Column: Waters ACQUITY UPLC HSS T3 1.8 µm 2.1 x 100 mm; A= H2O, B =MeOH

Results:

Compound		
UPLC-MSMS	Coconut charcoal 2g/6ml Test concentration of 100 µg/l	Coconut Charcoal Test concentration of 200 µg/l
1,4-dinitrosopiperazine	20.6 %	21.9 %
NDELA	0.0	0.0 %
NDEA	23.3 %	46.3 %
NDMA	0.0 %	126.7 %
NMOR	46.8 %	40.9 %
Nitrosopiperazine	0.0 %	0.0 %
NPIP	0.0 %	0.0 %

Conclusions:

No recoveries on NDELA, nitrosopiperazine, NPIP. NDMA not detected on 100 µg/l.

Test 12: Nitrosoamines, test of 6 SPE cartridges, UPLC-MSMS, HSF5 Column

Scope:	Nitrosamine concentration test, 6 different SPE cartridges, UPLC-MSMS, HS F5 Column, blank water matrix
Description:	Test of HLB, Easy, Envi, SDB, LiChrolut, Coconut Charcoal, blank water matrix SPE Cartridges: Merch **LiChrolut** EN 40-120 µm, 200 mg Waters Oasis **HLB** 30 µm, 6 ml/200 mg Macherey-Nagel Chromabond **Easy,** mean particle size 94 µm Supelco **Envi**-Carb 6 ml/250mg Supelco Coconut **Charcoal** J.T. Baker, Bakerbond SPE **SDB** 200 mg/6ml

1. Sample pH adjustment 6-7 (distilled water , no adjustment)
2. 100 ml sample, std. addition 100 µg/l + internal standard
3. SPE wash-up

   3 ml hexane
   3 ml DCM
   3 ml MeOH
   3 ml H2O

4. extraction into SPE slowly
5. drying
6. elution 5 ml DCM, 3 ml MeOH, 3 ml acetone (for coconut all volumes 2 x)
7. evaporation by TurboVap to 0,5 ml
8. addition of H2O to 10 % MEOH concentration
9. Internal standards 2 mg/l -> 25 µg/l, std 1 mg/l -> 50 µg/l

Column: Supelco Discovery HS F5, 150 mm x 2.1 mm, 3 µm.

Results:

Compound	HLB	Easy	SDP	LiChrolut	C8/ENVI	Coconut charcoal
NDELA	6 %	5 %	4 %	8 %	15 %	52 %
NMOR	40 %	61 %	51 %	78 %	123 %	31 %
Nitrosopiperazine	1 %	7 %	34 %	27 %		
1,4-dinitrosopiperazine	71 %	96 %	85 %	88 %	150 %	62 %
NDMA						
NDEA	47 %		7 %		27 %	26 %
NPIP	84 %	78 %	83 %	80 %	126 %	64 %
NDMA D6	99 %	117 %	132 %	5 %	62 %	118 %
Nitrosomorpholine D8	0 %	0 %	0 %	21 %	82 %	0 %
NDELA D8	0 %	0 %	0 %	0 %	0 %	0 %

Conclusions:

On the HSF5 column NDELA 50 % recovery on coconut charcoal, 30 % on Lichrolut and SDP, pH differs from previous tests.

Test 13: Nitrosoamines, test of 6 SPE cartridges, UPLC-MSMS, T3 Column

Scope:	Nitrosamine concentration test, 6 different SPE cartridges, UPLC-MSMS, T3 Column, blank water matrix
Description:	Test of HLB, Easy, Envi, SDB, LiChrolut, Coconut Charcoal, blank water matrix SPE Cartridges: Merch **LiChrolut** EN 40-120 µm, 200 mg Waters Oasis **HLB** 30 µm, 6 ml/200 mg Macherey-Nagel Chromabond **Easy,** mean particle size 94 µm Supelco **Envi**-Carb 6 ml/250mg Supelco Coconut **Charcoal** J.T. Baker, Bakerbond SPE **SDB** 200 mg/6ml

1. Sample pH adjustment 6-7 (distilled water , no adjustment)
2. 100 ml sample, std. addition 100 µg/l + internal standard
3. SPE wash-up

   3 ml hexane
   3 ml DCM
   3 ml MeOH
   3 ml H2O

4. extraction into SPE slowly
5. drying
6. elution 5 ml DCM, 3 ml MeOH, 3 ml acetone (for coconut all volumes 2 x)
7. evaporation by TurboVap to 0,5 ml
8. addition of H2O to 10 % MEOH concentration
9. Internal standards 2 mg/l -> 25 µg/l, std 1 mg/l -> 50 µg/l

Column: Waters ACQUITY UPLC HSS T3 1.8 µm 2.1 x 100 mm

Results:

Compound	HLB	Easy	SDP	LiChrolut	C8/ENVI	Coconut charcoal
NDELA	3 %	4 %		3 %	3 %	0,3 %
NMOR	0 %	33 %	0 %	45 %	34 %	3 %
Nitrosopiperazine	7 %		7 %	23 %		5 %
1,4-dinitrosopiperazine	92 %	87 %		174 %	260 %	1 %
NDMA		(755 %)	0 %			0 %
NDEA	28 %	71 %	0 %		0 %	37 %
NPIP	73 %	82 %	78 %	76 %	59 %	52 %
NDMA D6						
Nitrosomorpholine D8	0 %	0 %	0 %	7 %	0 %	0 %
NDELA D8	0 %	0 %	0 %	0 %	0 %	0 %

Conclusions:

On the T3 column NDELA no recovery over 4 % on any tested SPE cartridge. N-piperazine recoveries 23 % on LiChrolut and 7 % on SDP.

Pretreatment affects more on analysis where T3 is used (neutral eluents) than HSF5 (0.02 % acid). HSF5 is preferred other compounds but morpholine. In future HSF5 will be used also for nitrosamines.

Test 14: Nitrosoamines, test of SPE cartridges in series, UPLC-MSMS, HS F5 Column

Scope:	Nitrosamine concentration test, Coconut cartridge and LiChrolut in series, UPLC-MSMS, HS F5 Column, blank water matrix
Description:	Blank water matrix for nitrosoamines. SPE Cartridges: First: Supelco Coconut **Charcoal** 2 g Second: Merch **LiChrolut** EN 40-120 µm, 200 mg

1. Sample pH adjustment 6-7 (distilled water, no adjustment)
2. 100 ml sample, std. addition 100 µg/l + internal standard
3. SPE wash-up (volumes for coconut 2x)

   3 ml hexane
   3 ml DCM
   3 ml MeOH
   3 ml H2O

4. extraction into SPE slowly
5. drying by nitrogen
6. elution of both cartridges separately 5 ml DCM (one sample), 3 ml MeOH, 3 ml acetone , MeOH and acetone combined to second sample (for coconut all volumes 2 x)
7. evaporation by TurboVap to 0,5 ml
8. addition of MeOH to 10 % MEOH concentration

Column: Supelco Discovery HS F5, 150 mm x 2.1 mm, 3 µm.

a= 0,02 % HCOOH
b=0,02 % HCOOH/ACN

Results:	

No peaks on NDELA when DCM elution is used. Also lower recoveries on 1,4-dinitrosopiperazine (15 % DCM and 45 % on MeOH). Other detected from DCM portion.

Conclusions:	

Test 15: Nitrosoamines, Renewal test of SPE cartridges in series, UPLC-MSMS, HS F5 Column

Scope:	Nitrosamine concentration test, Coconut cartridge and LiChrolut in series, UPLC-MSMS, HS F5 Column, blank water matrix
Description:	Blank water matrix for nitrosoamines. SPE Cartridges: First: Supelco Coconut **Charcoal** 2 g Second: Merch **LiChrolut** EN 40-120 µm, 200 mg

1. Sample pH adjustment 6-7 (distilled water , no adjustment)
2. 100 ml sample, std. addition 100 µg/l + internal standard
3. SPE wash-up (volumes for coconut 2x)

   3 ml hexane
   3 ml DCM
   3 ml MeOH
   3 ml H2O

4. extraction into SPE slowly
5. drying by nitrogen
6. elution of both cartridges separately 5 ml DCM (one sample), 3 ml MeOH, 3 ml acetone , MeOH and acetone combined to second sample (for coconut all volumes 2 x)
7. evaporation by TurboVap to 0,5 ml
8. addition of MeOH to 10 % MEOH concentration

Column: Supelco Discovery HS F5, 150 mm x 2.1 mm, 3 µm.

a= 0,02 % HCOOH
b=0,02 % HCOOH/ACN

Results:	

Nitrosopiperazine recoveries 40 % from LiChrolut 200 mg MeOH/acetone extraction. Recovery from LiChrolut 500 mg about 15 % accordingly.

Conclusions:	

Test 16: Nitrosamine analysis, direct injection to UPLC-MSMS after dilution

Scope:	Nitrosamine analysis, direct injection to UPLC-MSMS after dilution
Description:	Analysis of selected solvent and wash water samples delivered by the Company

Wash water

Dilution factor	**Addition**
1000	internal standard to 100 µg/l
100	
10	
10	standard 30 µg/l + internal standard to 100 µg/l
10	standard 150 µg/l + internal standard to 100 µg/l

Solvent

Dilution factor	**Addition**
100 000	internal standard to 100 µg/l
10 000	
1 000	
1 000	standard 30 µg/l + internal standard to 100 µg/l
1 000	standard 150 µg/l + internal standard to 100 µg/l

Standards 1, 5, 10, 50, 100, 200 µl/l H2O
Column: Supelco Discovery HS F5, 150 mm x 2.1 mm, 3 µm.
Eluents: A= 0,01 % HCOOH, B= 0,02 % HCOOH/ACN. Inj. volume 5 µl.

Results:

Compound	**MDL mg/l, Wash water sample**	**Result mg/l, Wash water sample**	**MDL mg/l, Sol-vent sample**	**Result mg/l, Solvent sample**
Nitrosamines:				
1,4-dinitrosopiperazine	0.20	n.d.	20	n.d.
NDELA	0.01	<0.01	1.0	n.d.
NDEA	n.a.	n.a.	n.a.	n.a.
NDMA	n.a.	n.a.	n.a.	n.a.
NMOR	0.20	n.d.	20	n.d.
Nitrosopiperazine	0.01	n.d.	1.0	n.d.
NPIP	0.15	n.d.	15	n.d.
Alkylamines:				
DEN	0.05	n.d.	5.0	n.d.
DMA	0.05	n.d.	5.0	n.d.
EA	0.05	n.d.	5.0	n.d.
MMA	0.10	n.d.	50	n.d.
TEA	0.05	n.d.	5.0	n.d.
TMA	0.05	n.d.	5.0	n.d.
Solvent amines:				
AMP	0.05	n.d.	5.0	n.d.
DEA	0.05	1.2	5.0	11
EDA	10	n.d.	1.0	n.d.
MDEA	0.01	n.d.	1.0	n.d.
MEA	0.05	3 500	5.0	380 000
Piperazine	3.0	n.d.	300	n.d.

Conclusions:

On wash water samples MEA and DEA detected at quantifiable level. NDELA detected as trace amounts. Solvent sample MEA and DEA were quantified.
Some of the samples DEA contamination observed, results rejected.

Test 17: Formamide, acetamide, HPLC-RI with Shodex RSpakDE-413 column

Scope:	Test of formamide and acetamide, HPLC-RI, Column Shodex RSpakDE-413
Description:	
HPLC: Waters Alliance 2695 Std. solutions 10 mg/l and 100 mg/l Column Shodex RSpakDE-413 eluent KH2PO4 0,05 mlo/l pH 2.6 (adjusted by H3PO4) flow 1 ml/min RI-detector	
Results:	
No peaks.	
Conclusions:	
Other columns should be tested.	

Test 18: Formamide, acetamide, HPLC-RI with Boudapak C18 column

Scope:	Test of formamide and acetamide, HPLC-RI Column Bondapak C18
Description:	
HPLC: Waters Alliance 2695 Std. solutions 10 mg/l and 100 mg/l Column Bondapak C18 eluent KH2PO4 0,05 mlo/l flow 1 ml/min RI-detector, sensitivity 1024	
Results:	
Peaks detected, but at the side of the solvent peak.	
Conclusions:	
Other methods should be tested.	

Test 19: Formamide, acetamide, HPLC-MSMS, Cation exchange column

Scope:	Test of formamide and acetamide, part 1 HPLC-MSMS
Description:	
Waters HPLC-MSMS on scan mode Std. solutions 10 mg/l Column Dionex Cation exchance column eluent 50 % MeOH/0,5 % CH3COOH	
Results:	
No peaks.	
Conclusions:	
Other columns should be tested.	

Test 20: Formamide, acetamide, HPLC-RI, Nucleosil 100-5 SA Column, wash water and solvent samples

Scope:	Test of formamide and acetamide, HPLC-RI, Nucleosil 100-5 SA Column, wash water and solvent samples
Description:	
HPLC: Waters Alliance 2695 Std. solutions 100 mg/l, 200 mg/l and 500 mg/l Wash water G and solvent P samples delivered by the Company Column Shodex RSpakDE-413 eluent KH2PO4 0,05 mlo/l pH 2.6 (adjusted by H3PO4) flow 1 ml/min RI-detector	
Results:	
Both amides appear alongside the solvent peak with poor resolution. Standard compound addition into solvent and washwater samples gives poor response (interfering component at sample at the same RTT's).	
Conclusions:	
Other columns, eluents and analysis settings should be tested.	

Test 21: Formamide, acetamide, HPLC-RI, Bondapak C18 and Shodex DE- 413 Columns, wash water and solvent samples

Scope:	Test of formamide and acetamide, HPLC-RI, Bondapak C18 and Shodex DE- 413 columns, wash water and solvent samples
Description:	
HPLC: Waters Alliance 2695 Std. solutions 100 mg/l, 200 mg/l and 500 mg/l Wash water G and solvent P samples delivered by the Company Column Bondapak C18 Shodex DE- 413 eluent KH2PO4 0,05 mlo/l pH 2.6 (adjusted by H3PO4) flow 1 ml/min RI-detector	
Results:	
Both amides merge to the solvent peak.	
Conclusions:	
Not working. Other columns should be tested.	

Test 22: Acetaldehyde by HS-GC-MSD, wash water and solvent samples

Scope:	Test of acetaldehyde by HS-GC-MSD, wash water (2009-11-06) and solvent sample (2010-02-12)
Description:	
PerkinElmer HS-GC-MSD system HS: oven 30min@60°C, injection time 0,08 min, pressurize time 0,5 min, 22 psi He MSD: SIR m/z: 42, 43, 44 GC: init= 40°C hold 5 min, total run 5 min Salt addition of 1 g	
Results:	
Sample Wash water G (MEA about 0,5 %) acetaldehyde addition 1 mg/l, recovery **40 %** acetaldehyde addition 10 mg/l, recovery **34 %** Concentration of G sample: 0,32 mg/l, correceted 0,52 mg/l result: **< 1 mg/l** Solvent sample P (MEA about 30-40 %) sample dilution 10 x acetaldehyde addition 10 mg/l, recovery **8 %** sample dilution 100 x acetaldehyde addition 1 mg/l, recovery **34 %** sample dilution 100 x acetaldehyde addition 10 mg/l, recovery **36 %** Acetaldehyde concentration of the solvent sample **< 170 mg/l**	
Conclusions:	
It looks that MEA disturbs the analysis: MEA concentration in the sample 0,3-0,5 %, recovery of acetaldehyde 34-40 % MEA concentration in the sample 3-4 %, recovery of acetaldehyde about 10 % Detection limits: MEA concentration of 0,5 %, DL=2-5 mg/l MEA concentration of 30-40 %, DL=200-500 mg/l	

Test 23: Formaldehyde and acetaldehyde with DNPH-derivatization

Scope:	Determination of formaldehyde and acetaldehyde in aqueous samples
Description:	

Based on method presented in Journal of Chromatography A, 1216 (2009) 6554-6559

1. SPE cartridge LiChrolut EN 500mg/6ml (Merk) was conditioned by 5,0 ml of ACN and 10 ml of MQ-water.
2. pH of aqueous samples was adjusted to 1,5 with 1M HCl
3. 20 ml of 0,05 mg/ml DNPH-solution (derivatization solution) was loaded onto cartridge
4. 50 ml of sample was loaded on the cartridge
5. Aldehyde-derivatives were eluted with 7 ml of acetonitrile, first 2 ml was sent to waste.

Analysis by HPLC-UV at 360nm, µBONDAPAK C18 10µm 125Å 3,9×300mm column

Results:

Limit of detection for HPLC-UV was determined to be approximately 50µg/L (S/N=3) for both formaldehyde and acetaldehyde.
The instrumental method was tested to be linear at range 0,1-10mg/l.
The expected MEA (mono ethanolamine) concentration in the aqueous sample did not have an effect on this pre-treatment method. The spiked samples with and without MEA gave similar results. However pre-treated samples spiked with standard levels did not give linear results at the range 0,1-10 mg/L. This is hypothesized to be due to the cartridge capacity and/or the amount of derivatization solution. This issue remains to be tested.

Conclusions:

The method was found to be suitable for aqueous samples containing MEA. If the limit of detection needs to be lower, the method is easy to transfer to HPLC-MS. The issue of linearity of pre-treated standards can be solved with one or two simple tests. If this does not give acceptable results, also liquid-liquid extraction could be used.

Test 24: Nitrosoamines, LLE of NDMA, NDEA, NMOR, NPIP and DNPIPA on 5 % MEA matrix, GC-HRMS

Scope:	GC-HRMS determination of nitrosamines, characterization of the method
Description:	Liquid-liquid extraction of nitrosoamines NDMA, NDEA, NMOR, NPIP and DNPIPA, matrix 5 % MEA

Sample 500 ml of distilled water containing 5 % (V/V) of MEA, blank and standard additions ranging from 0.2 ng/L to 100 ng/L. Internal standards NDMA D6 and NMOR D8 at 20 ng/l. Three replicates at each level. Total number of samples was 18.

1. Extraction twice with dichlolomethane (total of 50 ml)
2. Wash-up of combined extracts with 50 ml of 1M HCl- solution
3. drying of the extract with anhydrous $NaSO_4$
4. evaporation by TurboVap to 0.5 ml
5. GC-HRMS analysis.

Columns Rxi-5Sil MS (30 m, 0.25 mm ID, 1.0 µm df) and Rtx-Dioxin2 (40m, 0.18 mm ID, 0.18 µm df) were tested with different resolutions to achieve optimum signal to noise ratio. Samples were finally run with Rtx-Dioxin2 column at a MS resolution of 8000.

Results:

NDMA and NMOR suffered from relatively high instrumental background and could only be detected at 0.2 - 0.5 µg/L. Other nitrosoamines could be detected below even 0.1 µg/L (corresponds to 0.1 ng/l in sample)
Recoveries of the internal standards (17 % for NDMA D6 and 47 % for NMOR D8) were lower than expected. The recoveries also showed significant deviation and good correction of all five nitrosoamines with the two internal standards available was not possible.
Due to relatively low recoveries the final detection limit was ≈ 1 ng/L in the conditions studied.

Conclusions:

The volatile nitrosoamines NDMA, NDEA, NMOR, NPIP and DNPIPA can be detrmined at ≈ 1 ng/L levels in samples containing 5 % MEA. However the deviation of the recoveries between different nitrosoamines would need to be better corrected for. The standards would need to be extracted as well or labelled internal standards for each nirtosoamine would need to be used.
Because of the very simple mass spectra (and low masses) these nitrosoamines have, a relatively high resolution must be used in MS-detection.

Test 25 Concentration of nitrosoamines by LLE, DCM extraction, GC-MSD, 0.5 % MEA

Scope:	Concentration of nitrosoamines in MEA solution by LLE
Description:	
Liquid-liquid extraction and purification of nitrosoamines using dichloromethane 6. Synthetic MEA samples (100 mL / 0,5 vol-%) spiked with 1 µg of nitrosoamines. 7. Also UHQ sample spiked with same amount of analytes and blank sample 8. LLE step done with 2 x 30 mL DCM 9. DCM phase washed once with 1 M HCl (100 mL) 10. Washed DCM phase dryed with N_2SO_4 and evaporated to 500 µL 11. Out of the 500 µL sample 100 µL used for GC analysis and rest of the sample switched to 1000 µL 10 % MeOH in UHQ Analysis by GC-MSD at SCAN-mode, HS5MS 30m, 0,25 µm, 0,25 mm column	
Results:	
The so called volatile nitrosoamines (Dnpz, NDEA, NDMA, NMOR, Npip) were primarily analysed with GC/MSD and recoveries indicated that LLE with LLE could be applied for a effective pre-treatment method. N-nitrosopiperazine and NDELA was to be analysed with UPLC-MS/MS but results showed that recoveries were extremely poor.	
Conclusions:	
LLE method is suitable for volatile nitrosoamines.	

Test 26 Concentration of nitrosoamines by LLE, DCM extraction, GC-MSD, 5 % MEA

Scope:	Concentration of nitrosoamines in MEA solution by LLE
Description:	
Liquid-liquid extraction and purification of nitrosoamines with different concentrations of MEA using dichloromethane 1. 3 x 100 mL synthetic MEA samples (0,5/2/5 vol-%) spiked with 1 µg of nitrosoamines. 2. LLE step done with 2 x 30 mL DCM 3. DCM phase washed once with 1 M HCl (60 mL) 4. Washed DCM phase dryed with N_2SO_4 and evaporated to 500 µL 5. Out of the 500 µL sample 100 µL used for GC analysis and rest of the sample switched to 1000 µL 10 % MeOH in UHQ Analysis by GC-MSD at SCAN-mode, HS5MS 30m, 0,25 µm, 0,25 mm column and UPLC-MS/MS with supelco HSF5 column	
Results:	
Results showed that the concentration of MEA within 0,5 % - 5 % has no effect on recoveries for volatile nitrosoamines as they were the same as previous test. The non-volatile part of nitrosoamines could not be detected with UPLC-MS/MS	
Conclusions:	
LLE method is suitable for volatile nitrosoamines for samples containing up to 5 % MEA	

Test 27 Concentration of nitrosoamines by LLE with pH adjustment of sample, 0.5 % MEA

Scope:	Concentration of nitrosoamines in MEA solution by LLE
Description:	
Liquid-liquid extraction and purification of nitrosoamines using dichloromethane 1. Synthetic MEA samples (2 x 100 mL / 0,5 vol-%) spiked with 1 µg of nitrosoamines. 2. First sample's pH was adjusted to 12,5 and second to 6,3 3. LLE step was done with 2 x 30 mL DCM 4. DCM phase washed once with 1 M HCl (50 mL) 5. Washed DCM phase dryed with N_2SO_4 and evaporated to 500 µL 6. Out of the 500 µL sample 100 µL used for GC analysis and rest of the sample switched to 1000 µL 10 % MeOH in UHQ Analysis by GC-MSD at SCAN-mode, HS5MS 30m, 0,25 µm, 0,25 mm column and UPLC-MS/MS with supelco HSF5 column	
Results:	
The results showed that no major effect for recoveries was observed within different pH values as recoveries were the same as before. The non-volatile part of nitrosoamines could not be detected by UPLC-MS/MS	
Conclusions:	
LLE method is suitable for volatile nitrosoamines regardless of sample pH between 6.3-12.5	

Test 28 Concentration of nitrosoamines by LLE, 5 % MEA

Scope:	Concentration of nitrosoamines in MEA solution by LLE
Description:	

Liquid-liquid extraction and purification of nitrosoamines using dichloromethane

1. Synthetic MEA samples (2 x 100 mL / 5 vol-%) spiked with 1 µg of nitrosoamines.
2. pH adjustment to 6,1 and 12,1
3. LLE step done with 2 x 30 mL DCM
4. DCM phase washed once with 1 M HCl (50 mL)
5. Washed DCM phase dryed with N_2SO_4 and evaporated to 500 µL
6. Out of the 500 µL sample 100 µL used for GC analysis and rest of the sample switched to 1000 µL 10 % MeOH in UHQ

Analysis by GC-MSD at SCAN-mode, HS5MS 30 m, 0,25 µm, 0,25 mm column and UPLC-MS/MS with supelco HSF5 column

Results:	

Recoveries were still at the same level as before and very little or no effect was observed within these parameters

Non-volatile nitrosoamines are not detected with UPLC-MS/MS

Conclusions:	

LLE method is suitable for volatile nitrosoamines the non-volatiles are still a problem

Test 29 Concentration of nitrosoamines by LLE, 5 % MEA, salt addition

Scope:	Concentration of nitrosoamines in MEA solution by LLE focus on non-volatile nitrosoamines
Description:	

Liquid-liquid extraction and purification of nitrosoamines using dichloromethane. Addition of NaCl to saturation point for improving recoveries for N-nitrosopiperazine and NDELA

1. 3 x 100 mL of synthetic MEA sample (5 vol-%) spiked with 1 µg of nitrosoamines.
2. 2 x 100 mL UHQ sample with 1 µg of nitrosoamines (other with NaCl and other without)
3. Adjustment of pH to 6,5/12,5/11,3 (except for UHQ sample)
4. Addition of NaCl to saturation point
5. LLE step done with 2 x 30 mL DCM
6. DCM phase washed once with 1 M HCl (50 mL) (except for UHQ sample)
7. Washed DCM phase dryed with N_2SO_4 and evaporated to 500 µL (except for UHQ sample)
8. Out of the 500 µL sample 100 µL used for GC analysis and rest of the sample switched to 1000 µL 10 % MeOH in UHQ

UPLC-MS/MS with supelco HSF5 column

Results:	

The maximum recovery for non-volatile nitrosoamines was achieved from UHQ sample with NaCl but the recoveries still peaked at 1 % for N-nitrosopiperazine and 0,7 % for NDELA

Conclusions:	

LLE is not suitable for NDELA and N-nitrosopiperazine whilst using DCM

Test 30 Concentration of nitrosoamines by LLE with different solvents (DEE, IPE, EA)

Scope:	Concentration of nitrosoamines from UHQ by LLE focus on non-volatile nitro-soamines
Description:	

Liquid-liquid extraction and purification of nitrosoamines using different organic solvents

1. UHQ water samples (3 x 100 mL) spiked with 1 µg of nitrosoamines.
2. Selected solvents diethyl ether (DEE), isopropyl ether (IPE) and ethyl acetate (EA)
3. LLE steps were done with 2 x 30 mL
4. HCl wash –step was not done
5. The whole sample was used for UPLC analysis

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries %	**DEE**	**IPE**	**EA**
NDELA	<LOD	<LOD	5,2*
N-nitrosopiperazine	<LOD	<LOD	1,3*

*Ethyl acetate evaporated to dryness but was still analysed

Conclusions:

Liquid-liquid extraction for non-volatile nitrosoamines is a challenging task but ethyl acetate will be investigated further with different parameters

Test 31 Concentration of nitrosoamines by LLE, EA at different pH & salt

Scope:	Concentration of nitrosoamines in MEA solution by LLE using ethyl acetate focus on non-volatile nitrosoamines
Description:	

The use of ethyl acetate as an LLE solvent was further investigated with different parameters and from 5 % MEA solution

1. 4 x 100 mL samples of 5 % MEA in UHQ spiked with 1 µg of analytes
2. Two of the samples were pH-adjusted to 6,1 and 12,8 third was left untreated and fourth untreated with saturated NaCl
3. Eluted with ethyl acetate 2 x 30 mL
4. The whole sample was used for UPLC analysis

UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries %	**5 % MEA pH 6,1**	**5 % MEA pH 12,8**	**5 % MEA**	**5 % MEA + NaCl**
NDELA	4,6	1,1	1,5	<LOD
N-nitrosopiperazine	<LOD	4,8	4,0	4,8

Conclusions:

NDELA behaves differently from N-nitrosopiperazine in alternating ph-values but all the recoveries are unacceptable. It seems that LLE for these two compounds is difficult to apply. SPE methods will be investigated.

Test 32 Concentration of nitrosoamines by SPE, NDELA and N-nitrosopiperazine

Scope:	Concentration of nitrosoamines in MEA solution by SPE focus on non-volatile nitrosoamines
Description:	

Solid phase extraction specially for NDELA and N-nitrosopiperazine from solution containing MEA with Merck LiChrolut EN (200 mg/6mL) and Supelco Coconut Charcoal (2g/6mL)

1. Synthetic MEA sample (100 mL / 5 vol-%) spiked with 1 µg of nitrosoamines.
2. Adjustment of pH to 6,1 with formic acid
3. Cartridge clean-up with hexane, DCM, MeOH and UHQ
4. Coconut charcoal and LiChrolut connected in series (coconut on top)
5. Sample addition and drying with N_2
6. Elution of cartridges separately: LiChrolut MeOH and acetone and coconut with DCM, MeOH, Asetone and hexane
7. Evaporation of solvents and solvent switch to 1000 µL 10 % MeOH in UHQ

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:	

The evaporation of elute from coconut charcoal produced thick but clear liquid, which was thought to be MEA. It could not be injected to UPLC so a DCM wash of this liquid was applied and the DCM was evaporated and switched to 10 % MEA and analysed. This DCM wash step gave recoveries for NDELA and Nitrosopiperazine 10 % and 1 % respectively. The elute from LiChrolut EN had no detectable amounts of these analytes.

Conclusions:	

Coconut charcoal probably concentrates MEA and makes it difficult to analyse nitrosoamines with these parameters and with this cartridge type. LiChrolut EN seems not to have same kind of retention for MEA.

Test 33 Concentration of nitrosoamines by SPE, NDELA and N-nitrosopiperazine, pH

Scope:	Concentration of nitrosoamines in MEA solution by SPE focus on non-volatile nitrosoamines
Description:	

Solid phase extraction specially for NDELA and N-nitrosopiperazine from solution containing MEA with Merck LiChrolut EN (500 mg/6mL) and Supelco Coconut Charcoal (2g/6mL)

1. Synthetic MEA samples (4 x 50 mL / 5 vol-%) spiked with 1 µg of nitrosoamines.
2. Adjustment of pH (2 x 3,7; 1x 6,8 and 1 x 6,0) with formic acid
3. Cartridge clean-up with hexane, DCM, MeOH and UHQ
4. Sample addition separately to each cartridge and drying with N_2
5. Elution of cartridges separately with different solvents (EA, MeOH, acetone)
6. Evaporation of each solvent separately and solvent switch to 1000 µL 10 % MeOH in UHQ

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries (coconut cc)% pH 3,7	**EA**	**MeOH**	**Acetone**
NDELA	13	<LOD	8,3
N-nitrosopiperazine	<LOD	<LOD	<LOD

Recoveries (coconut cc) % pH 6,8	**EA**	**MeOH**	**Acetone**
NDELA	9	<LOD	8,3
N-nitrosopiperazine	1,5	<LOD	<LOD

Recoveries (LiChrolut EN) % pH 3,7	**EA**	**MeOH**	**Acetone**
NDELA	28,4	<LOD	<LOD
N-nitrosopiperazine	6,7	<LOD	<LOD

Recoveries (LiChrolut EN) % pH 6,0	**EA**	**MeOH**	**Acetone**
NDELA	50	<LOD	<LOD
N-nitrosopiperazine	21,5	<LOD	<LOD

Conclusions:

Out of these two cartridges LiChrolut EN alone works best for the both of analytes. Recovery for NDELA is quite acceptable but N-nitrosopiperazine would need an individual labelled standard to be suitable.

Test 34 Concentration of nitrosoamines by LiChrolut EN SPE, NDELA and N-nitrosopiperazine

Scope:	Concentration of nitrosoamines in MEA solution by SPE focus on LiChrolut EN cartridge and non-volatile nitrosoamines
Description:	

Solid phase extraction specially for NDELA and N-nitrosopiperazine from solution containing MEA with Merck LiChrolut EN (500 mg/6mL)

1. Synthetic MEA samples (4 x 50 mL / 5 vol-%) spiked with 1 µg of nitrosoamines.
2. Each sample adjusted to different pH value (4,7/8,6/9,9/11,7)
3. Cartridge clean-up with hexane, DCM, MeOH and UHQ
4. Sample addition and drying with N_2
5. Elution of cartridges separately with EA and MeOH + Acetone
6. Evaporation of both eluents separately and solvent switch to 1000 µL 10 % MeOH in UHQ

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries % pH 4,7	**EA**	**MeOH + acetone**
NDELA	52	<LOD
N-nitrosopiperazine	10,7	<LOD

Recoveries % pH 8,6	**EA**	**MeOH + acetone**
NDELA	33,5	<LOD
N-nitrosopiperazine	38,3	<LOD

Recoveries % pH 9,9	**EA**	**MeOH + acetone**
NDELA	1,3	<LOD
N-nitrosopiperazine	18,3	<LOD

Recoveries % pH 11,7	**EA**	**MeOH + acetone**
NDELA	<LOD	<LOD
N-nitrosopiperazine	8,1	<LOD

Conclusions:

Retention efficiency changes drastically with different pH values. This is especially evident with NDELA. It can also be observed that ethyl acetate elutes all detectable amounts of analytes from the cartridge. The peak retention efficiency does not occur at the same pH value for these two compounds.

Test 35 Concentration of nitrosoamines and alkylamines by SPE

Scope:	Concentration of nitrosoamines in MEA solution by SPE focus on LiChrolut EN cartridge and non-volatile nitrosoamines trial concentration of alkylamines

Description:

Solid phase extraction specially for NDELA and N-nitrosopiperazine from solution containing MEA with Merck LiChrolut EN (500 mg/6mL). Addition of alkylamines to sample.

1. Synthetic MEA (5 vol-%) samples (1 x 100 mL and 1 x 500 mL) spiked with 1 µg of nitrosoamines and alkylamines.
2. pH adjusted to 6,9 (a compromise between NDELA and nitrosopiperazine)
3. Cartridge clean-up with hexane, DCM, MeOH and UHQ
4. Sample addition and drying with N_2
5. Elution of cartridges with EA for nitrosoamines and additional elution with MeOH and acetone for alkylamines
6. Evaporation of eluents and solvent switch to 1000 µL 10 % MeOH in UHQ

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries for nitrosoamines %	**100 mL**	**500 mL**
NDELA	19,6	3,4
N-nitrosopiperazine	34,5	10,6

Results implied that with these parameters LiChrolut EN was not the cartridge of choice for alkylamines as only diethylamine and triethylamine could be detected from 100 mL sample eluted with MeOH with recoveries 9,3 and 7,6 % respectively.

Conclusions:

LiChrolut EN works as expected up to sample volume of 100 mL. Increasing sample volume to 500 mL significantly lowers the recovery percent. Alkylamines needs propably different type of SPE cartridge as it is not expected that changes in sample variables will increase recovery with LiChrolut EN (other than di- and triethylamine).

Test 36 Concentration of alkylamines by different SPE cartridges

Scope:	Concentration of alkylamines in MEA solution by SPE mapping of retention efficiencies of different types of SPE cartridges

Description:

Different SPE cartridges were tested which might have some retention efficiency for small polar compounds as alkylamines. Cartridges of choice were: LiChrolut EN, Coconut charcoal, Waters OASIS MCX (500 mg/6mL) and Waters OASIS WCX (150 mg/6 mL)

Five 50 mL samples of 5 vol-% MEA was prepared from UHQ. pH for all samples were adjusted to meet the demands of different cartridges: Sample for LiChrolut EN was adjusted to 12,4 as it was known that at pH value of 6,9 retention was poor. Coconut charcoal was adjusted to 4,6 as it was known that at in alkaline conditions MEA tends to jam the cartridge. With MCX two different pH values were used 3,4 and 6,5. The pH for WCX had to be more alkaline than 7 so 11,3 was tested.

For LiChrolut and coconut procedure was as mentioned before but for MCX and WCX procedure was as follows:

1. Cartridge clean-up with MeOH and UHQ for MCX and MeOH and slightly alkaline UHQ for WCX
2. Addition of sample
3. Wash step with 2% formic acid in UHQ and MeOH for MCX and none for WCX at this stage
4. Elution with 2,5 % NH_4OH in MeOH for MCX and 2% HCOOH in MeOH for WCX (In addition elution of possible samples from WCX was assured with second elution step with 2 % HCOOH in mixture of MeOH/DCM/Hexane/Ethyl acetate

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries %	**LiChrolut EN**	**Coconut charcoal**	**Oasis MCX 3,4 / 6,5**	**Oasis WCX**
Methylamine	<LOD	<LOD	<LOD	<LOD
Dimethylamine	0,9 (Acetone)	<LOD	<LOD	1,4 (MeOH)
Trimethylamine	<LOD	<LOD	<LOD	<LOD
Ethylamine	<LOD	<LOD	<LOD	<LOD
Diethylamine	44 (DCM)	26 (MEOH)	21 / 28	11,5 (MeOH)*
Triethylamine	44,6 (DCM)	62,8 (MeOH)	3,7 / 5,7	56 (MeOH)

*peak partly outside of windowed area

Conclusions:

LiChrolut EN was the best cartridge for di- and triethylamine as it produced best peak shapes and decent recoveries. Although MCX and WCX –methods might benefit from parameter optimization.

Test 37 Concentration of alkylamines by SPE and LLE, 5 % MEA

Scope:	Concentration of alkylamines in very alkaline conditions with LLE and SPE
Description:	

Different SPE cartridges were tested in very alkaline conditions and compared to LLE in equally alkaline conditions. In all eight 100 mL synthetic samples of 5 vol-% MEA in UHQ was made and 1 µg of alkylamine standards was added. Sodium hydroxide in granular form was added to saturation point. Four of the samples were extracted with LLE using hexane, ethyl ether, dichloromethane and ethyl acetate. Identical samples were extracted using four different SPE cartridges: Coconut CC, C18 (supelco discovery), Oasis HLB (Waters) and Envi-Carb (Supelco)

LLE was always done with 2 x 30 mL of solvent which was evaporated to smaller volume with TurboVap and switched to 10 % MeOH in UHQ (1000 µL). SPE cartridges were conditioned with MeOH and UHQ and eluted consecutive with DCM and MeOH.

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

LLE Recoveries %	**Hexane**	**Ethyl ether**	**Dichloro-methane**	**ethyl acetate**
Methylamine	<LOD	<LOD	<LOD	<LOD
Dimethylamine	<LOD	<LOD	<LOD	<LOD
Trimethylamine	<LOD	<LOD	<LOD	<LOD
Ethylamine	<LOD	<LOD	<LOD	<LOD
Diethylamine	<LOD	7	20	<LOD
Triethylamine	4,8	7,6	28,9	<LOD

SPE Recoveries %	**Coconut**	**C18***	**HLB**	**Envi-Carb**
Methylamine	<LOD	<LOD	<LOD	<LOD
Dimethylamine	<LOD	<LOD	<LOD	<LOD
Trimethylamine	<LOD	<LOD	<LOD	<LOD
Ethylamine	<LOD	<LOD	<LOD	<LOD
Diethylamine	<LOD	<LOD	13	<LOD
Triethylamine	12,4 (DCM)	4,5 (DCM)	7,6 (DCM)	<LOD

*C18 was operated well above its normal pH range so it was destroyed when MeOH was added for the second elution.

Conclusions:

Concentration of other alkylamines than di- and triethylamine is not straightforward operation. For di- and triethylamines LLE and SPE can propably be implemented.

Test 38 Concentration of alkylamines SPE and LLE, 2 % MEA

Scope:	Concentration of alkylamines in acidic conditions with LLE and SPE
Description:	

Different SPE cartridges and combination of cartridges was tested for synthetic (MEA 2 vol-%) samples acidified with formic acid. In all ten 100 mL synthetic samples were made and 1 µg of alkylamine standards was added. Four of the samples were extracted with LLE using hexane, ethyl ether, dichloromethane and ethyl acetate at pH of 4,8. SPE samples were all in the pH of 7,3 except for MCX which was at pH of 4,8. Other cartridges were LiChrolut EN, Coconut CC in series with WCX and MCX (Coconut on top), Envi-Carb, HLB, MCX and WCX

LLE and SPE was performed exactly as mentioned before except for WCX cartridge which was only eluted with 2 % HCOOH in MeOH

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

LLE Recoveries %	**Hexane**	**Ethyl ether**	**Dichloro-methane**	**ethyl acetate**
Methylamine	<LOD	<LOD	<LOD	<LOD
Dimethylamine	<LOD	<LOD	<LOD	<LOD
Trimethylamine	<LOD	<LOD	<LOD	<LOD
Ethylamine	<LOD	<LOD	<LOD	<LOD
Diethylamine	<LOD	<LOD	<LOD	<LOD
Triethylamine	<LOD	<LOD	<LOD	<LOD

SPE Recoveries %	**Coconut + WCX/MCX**	**LiChrolut EN**	**Oasis HLB**	**MCX**	**WCX**	**Envi-Carb**
Methylamine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Dimethylamine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Trimethylamine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ethylamine	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Diethylamine	47,2 (Coconut, MeOH) 1,6 (MCX)	<LOD	<LOD	2,1	1,7	<LOD
Triethylamine	47,2 (Coconut, MeOH)	16,2 (MeOH) 16,2 (DCM)	<LOD	5	2,3	<LOD

Conclusions:

It was thought that cocnut charcoal on top of WCX and MCX would remove some of the interfering MEA but it did not realise in recoveries for the WCX and MCX cartridges.

Test 39 Loss of alkylamine analytes during evaporation

Scope:	Loss of alkylamines on evaporation step of the pretreatment procedure
Description:	

Evaporation step of the pretreatment procedure was simulated by injecting 1 µg of alkylamines to 20 mL of three types of MeOH: Neutral, acidic and alkaline and evaporated with TurboVap so that the end result was 1000 µL of 10 % MeOH in UHQ.

Analysis by UPLC-MS/MS with supelco HSF5 column

Results:

Recoveries %	**Acidic MeOH**	**Neutral MeOH**	**Alkaline MeOH**
Methylamine	<LOD	27,8	31
Dimethylamine	<LOD	21,5	35,6
Trimethylamine	59,0	1,1	0,7
Ethylamine	<LOD	28,7	41,1
Diethylamine	41,5	28,3	52,5
Triethylamine	48,9	18,0	29,4

Conclusions:

It can be seen that trimethylamine is the most sensitive to evaporation step which propably explains why it has not been able to be concentrated even from UHQ water. The reason why methylamine, dimethylamine and ethylamine can not be detected from acidic MeOH is thought to be caused by the shift in retention time which in turn is caused by pH value.

Test 40 Alkylamines by purge and trap separation from MEA and UHQ water

Scope:	Concentration and clean-up of MEA from sample matrix
Description:	Three impinger vials, 2 % MEA test, 500 ml->50ml->50ml and UHQ test 50ml->50ml->50ml were connected in series. Nitrogen was used as a purge gas. On MEA test samples were taken from the last two impingers. On UHQ test I sample was taken from the first impinger vial after 45 min. at room temperature On UHQ test II sample was taken from the first impinger vial after 45 min. at 60°C On UHQ test III sample was not analysed because of high salt concentration UHG water trapping solution contains total recovery of the second and third vials used by trapping on UHQ test.

Alkalic 2 vol-% MEA-solution 500 ml, spiked with alkylamines and a revovery test from UHQ water with different treatment parameters

2 vol-% MEA in room temperature

1. Purged with N_2 and trapped to 50 ml 0,1M HCl
2. Concentration of spiked sample: 20 µg/L
3. Theoretical complete recovery 200 µg/L
4. Direct analysis of trapping solution by UPLC-MSMS

UHQ water

1. 50 mL UHQ sample spiked to 200 µg/L with alkylamines
2. pH adjusted to 12,6
3. Trapping solution 50 mL of 0,1 M HCl
4. Experiment divided into different steps:
   - I. Purging in room temperature for 45 min and sampling from both vials
   - II. Heating added (60 °C) for next 45 min and sampling from both vials
   - III. Addition of salts of NaCl and K_2SO_4 until saturation purging for 45 min and sample taken from trapping solution
5. Samples analysed directly with UPLC-MSMS

Results:

Recoveries % from initial concentration	**2 vol-% MEA trapping solution**	**UHQ water sample from the solution under purge after I (45 min@20°C)/ after II(45 min@60°C)**	**UHQ water, trapping solutions**
Methylamine (MMA)	<LOD	100 / 36	18
Dimethylamine (DMA)	<LOD	100 / 6	27
Trimethylamine (TMA)	<LOD	72 / <LOD	57
Ethylamine (EA)	<LOD	106 / 9,2	27,7
Diethylamine (DEN)	<LOD	86 / <LOD	23,7
Triethylamine (TEA)	<LOD	64,8 / <LOD	17

Conclusions:

The ambient temperature used for 2 vol-% MEA solution was propably not enough to remove any analytes from sample solution.
All analytes could be purged to some extent from UHQ water when heat was added. The addition of salts did not have any effect on purging efficiency. Some losses of analytes was observed which may be because of insufficient trapping to 0,1 M HCl.

Test 41 Alkylamines by purge and trap separation from MEA, AMP, DEA solution

Scope:	Concentration and clean-up of MEA from sample matrix
Description:	

Alkalic 2,5 vol-% MEA/1 vol-% MDEA/0,5 vol-% AMP/0,5 vol-% DEA -solution 200 ml, spiked with alkylamines 1 µg and a recovery test from UHQ water were made. Sample container was eated in ultrasound bath at 66 ºC for 45 minutes. Traps 2 x 25 mL of 0.1 M HCl were kept in water bath at 10 ºC.

The UHQ water sample was ruined by overflowing caused by ultrasound bath and possible contamination occurred to trap solution so it was discarded.

Results:

Recoveries %	**Solvent amine trapping solution**
Methylamine (MMA)	<LOD
Dimethylamine (DMA)	<LOD
Trimethylamine (TMA)	90
Ethylamine (EA)	<LOD
Diethylamine (DEN)	43
Triethylamine (TEA)	54

Conclusions:

Recoveries for trimethyl-, diethyl- and triethylamine gave quite good recoveries also for dimethyl- and ethylamines some poor peaks were detected but quantification was impossible. Also purging gas was not constant during the experiment so experiment should be done again. Before any conclusions can be drawn.

Test 42 Alkylamines by purge and trap

Scope:	Concentration and clean-up of MEA from sample matrix
Description:	

Alkalic 2,5 vol-% MEA/1 vol-% MDEA/0,5 vol-% AMP/0,5 vol-% DEA -solution 200 ml, spiked with alkylamines 1 µg was made. Sample container was held in ultrasound bath at 66 ºC for 45 minutes. Traps 2 x 25 mL of 0,1 M HCl were kept in water bath at 10 ºC.

Test was ruined because the ultrasound bath malfunction during the experiment.

Results:

Recoveries %	**Solvent amine trapping solution**
Methylamine (MMA)	<LOD
Dimethylamine (DMA)	<LOD
Trimethylamine (TMA)	120
Ethylamine (EA)	<LOD
Diethylamine (DEN)	<LOD
Triethylamine (TEA)	<LOD

Conclusions:

It is possible to liberate some of the alkylamines from sample matrix containing MEA but ultra-sound is needed to get others than trimethylamine from sampling solution.

Test 43 Ion-pair extraction of alkylamines with BEHPA

Scope:	Ion-pair extraction of alkylamines from synthetic sample matrix containing MEA
Description:	
LLE was tested by formation of an ion-pair with BEHPA (bis-2-ethylhexyl phosphate). Ion-pair reagent was diluted in chloroform. 2 % MEA solution was tested with spiked alkylamines.	
Results:	
Conclusions:	
Experiment failed. The chloroform phase became very thick and oily, maybe because of MEA	

Test 44 Concentration of alkylamines SPE, different MEA concentrations

Scope:	Concentration of alkylamines in acidic conditions with LLE and SPE
Description:	

Different concentrations of MEA (0,1 %/0,5 %/1 %/2 %) were tested with cation exchange SPE cartridges (WCX and MCX)

Total of eight 100 mL synthetic samples were made and spiked to 500 ng/L concentrations of alkylamines. Four were extracted with MCX and four with WCX. In addition two samples was done with more alkaline pH than normally is used (10,7) into 2 % MEA.

Results:

SPE Recoveries %	**MCX 0,1 %/ 0,5 %/ 1 %/ 2 %/ph 10,7**	**WCX 0,1 %/ 0,5 %/ 1 %/ 2 %/ pH 10,7**
Methylamine	<LOD	<LOD
Dimethylamine	<LOD	<LOD
Trimethylamine	<LOD	<LOD
Ethylamine	<LOD	<LOD
Diethylamine	<LOD*	<LOD*
Triethylamine	50 / 22,5 / <LOD** / 20 / 22,5	25 / 10 / <LOD**/ <LOD / 32,5

*Problems with background reason yet unknown
**pH adjustment test was done with these samples which caused dilution of sample.

Conclusions:

Recoveries only for Triethylamine