SINTEF REPORT

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TITLE	
H&ETQP Amine1, Call-off 2: **Verify manual sampling procedures**	
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ABSTRACT

The objective of H&ETQP/Amine1 call-off 2 is to have well documented analytical procedures for sampling, sample preparation and analysis of specific analytes in flue gas, wash water and amine solvent from post combustion amine based CO_2 capture in order to enable complete emission characterization.

Results: The results of this project are six procedures which are given as six appendices to this report. Each procedure covers capture of analyte, sample preparation and instrumental analysis for 1) nitrosamines, 2) nitramines, 3) solvent amines, 4) alkylamines (including ammonia), 5) aldehydes and 6) total nitrosamines. The report describes and discusses the rationale behind the suggested methodology and presents results that are used as basis for the development and testing of the methodology. The report also identifies and discusses factors that are critical for the performance of the given methodology.

Conclusions: 1) Sampling / capture of analyte: A complete system for isokinetic sampling is suggested that utilizes a) cooled probe followed by b) a condenser followed by c) four gas wash bottles in series for trapping of analytes. The system is based on commercially available units and components. 2) An overall sample procedure and a process flow diagram are given. Two complementary extraction procedures based on liquid-liquid-extraction (LLE) and solid phase extraction (SPE) are given as central parts of the procedure. 3) Analytical procedures are given for the following analytes: Nitrosamines (N-Nitrosodimethylamine (NDMA), N-Nitrosodiethylamine (NDEA), N-Nitrosomorpholine (NMOR), N-Nitrosopiperidine (NPIP), N-Nitrosoethanolamine (NDELA), N-Nitrosopiperazine (NPZ), 1,4-Dinitrosopiperazine (DNPZ)), nitramines: (MEA-nitramine, AMP-nitramine, piperazine-nitramine), solvent amines (MEA, DEA, AMP, piperazine), alkylamines (methylamine, ethylamine, dimethylamine, diethylamine), aldehydes (formaldehyde, acetaldehyde), ammonia and total nitrosamines.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
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SELECTED BY AUTHOR	CO_2 capture	CO_2 innfanging
	Environment	Miljø
	Analytical methods	Analysemetoder

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Executive summary

The objective of H&ETQP/Amine1 call-off 2 is to have well documented analytical procedures for sampling, sample preparation and analysis of specific analytes in flue gas, wash water and amine solvent from post combustion amine based CO_2 capture in order to enable complete emission characterization.

The following analytes are within the scope of this project: Nitrosamines (N-Nitrosodimethylamine (NDMA), N-Nitrosodiethylamine (NDEA), N-Nitrosomorpholine (NMOR), N-Nitrosopiperidine (NPIP), N-Nitrosoethanolamine (NDELA), N-Nitrosopiperazine (NPZ), 1,4-Dinitrosopiperazine (DNPZ)), nitramines: (MEA-nitramine, AMP-nitramine, piperazine-nitramine), solvent amines (MEA, DEA, AMP, piperazine), alkylamines (methylamine, ethylamine, dimethylamine, diethylamine), aldehydes (formaldehyde, acetaldehyde), ammonia and total nitrosamine.

The *combined cold probe – condenser – liquid absorption system* represents an integrated sampling system for isokinetic sampling that has several advantages compared to a classic liquid absorption-only systems employing either gas wash bottles or impingers. For the purposes given in the scope of this project, this system is suggested and recommended for the integrated sampling of the analytes given in the scope.

The suggested *overall procedure for sample preparation* covers the analytes given in the scope of work. Although the main target matrix in this study is flue gas, the procedures given for sample preparation is also valid for wash water and MEA solvent. Two complementary *extraction procedures based on liquid-liquid-extraction (LLE) and solid phase extraction (SPE)* are given as central parts of the procedure. Work remains for full verification and validation of the sample preparation methodologies.

Mass spectrometric methodology has been developed that cover the list of analytes given in the scope. The methods are based on liquid chromatography with triplequadrupole mass spectrometry (LC-MS-MS-QQQ) for nitrosamines, nitramines, amines and aldehydes, on gas chromatography with mass spectrometry (GC-MS) for the alkylamines and ammonia and on gas chromatography with chemiluminescence detection (GC-MS-NCD) for total nitrosamines. The analytical methods have been adapted to the procedures for sampling (capture of analyte) and sample preparation (work-up). Overall method uncertainty needs confirmation and experimental verification.

Background

The CO_2 Capture Mongstad (CCM) Project is in an early development phase of project development. The project is at the moment organized as a joint effort by Gassnova SF (Company) and Statoil, and is funded by the Norwegian government. The purpose of the project is to plan and build a large scale CO_2 capture plant (the CCP). The facility will be situated next to the Mongstad Refinery on the Mongstad industrial site north of Bergen on the west coast of Norway.

An amine based CO_2 capture plant may potentially cause harmful emissions to the atmosphere. Amines and degradation products from reactions in the process and in the atmosphere are of particular concern, but there is limited knowledge about the behaviour of these chemical compounds.

1   Objectives

The objective of H&ETQP/Amine1 call-off 2 is to have well documented analytical procedures for sampling, sample preparation and analysis of specific analytes in flue gas, wash water and amine solvent from post combustion amine based CO_2 capture in order to enable complete emission characterization.

2   Scope of work

The scope of work of this project is to perform experimental work to develop procedures for sampling (capture of analyte), sample preparation (sample workup) and analysis (instrumental analysis).

The analytes to be covered by the procedures are:

Nitrosamines
  N-Nitrosodimethylamine (NDMA)
  N-Nitrosodiethylamine (NDEA)
  N-Nitrosomorpholine (NMOR)
  N-Nitrosopiperidine (NPIP)
  N-Nitrosoethanolamine (NDELA)
  N-Nitrosopiperazine (NPZ)
  1,4-Dinitrosopiperazine (DNPZ)

Nitramines
  MEA-nitramine
  AMP-nitramine
  Piperazine-nitramine

Solvent amines
  Monoethanolamine (MEA)
  Diethanolamine (DEA)
  2-Amino-2-metyl-1-propanol (AMP)
  Piperazine (PZ)

Alkylamines
  Methylamine
  Ethylamine
  Dimethylamine
  Diethylamine

Aldehydes
  Formaldehyde
  Acetaldehyde

Ammonia

Total nitrosamines

3 Results

The deliverables from this study are the written procedures for sampling, sample preparation and analysis of the compounds listed above. The procedures are given as attachments (Appendices 1 to 6) to this report.

3.1 Sampling methodology (capture of analyte)

For an in-depth description of sample point design, procedures for sampling and online analysis we refer to the reports from Wittgens, et.al. 2010[1], Wittgens, et.al. 2010[2] and Wittgens, et.al. 2010[3], respectively. An overview of the compounds of interest and their physical properties are given in Wittgens, et.al. 2010. The boiling points of the compounds given in reference 2 and 3 range from app. -30°C to in excess of 280°C, this in combination with thermal instability of several compounds defines the operation range for the sampling device.

3.2 Gas sampling methods

This report refers to two separate experiments that have high relevance for the results presented here. The VOCC (Validation Of Carbon Capture) experiment performed in call-off 1 and the Esbjerg Emission Campaign performed in call-off 2, these two experiments are complementary to each other. In the VOCC experiment a controlled stream of flue gas was produced based upon known concentrations of nitrosamines, amines, ammonia and alkylamines in the wash water section. This flue gas stream was used for comparison of three different sampling systems. In the Esbjerg campaign, two of the systems (the ISOK4 and the Cold trap) were used identically to the VOCC experiment, except that the ISOK4 gas wash bottles were replaced by impingers. Further a system (MOLAB system) consisting of a heated probe with three parallel wash bottle trains (the first gas wash bottle for condensation was always empty at start, the two following wash bottles were filled with various liquid absorbents) was utilized. This configuration made it possible to perform sampling in different absorption solutions in parallel.

3.2.1 VOCC experiment

Three different methodologies (all iso-kinetically operated) for gas sampling was applied during the VOCC-experiment[4]:

- **"ISOK4":** cooled probe and train of gas washing bottles with acidic absorption solution, the first bottle is empty and used as liquid collector and gas cooler.
- **"Impinger":** short probe (no cooling) and train of impinger bottles with acidic absorption solution; last bottle empty to avoid droplet carry over.
- **"Cold-trap":** collection of condensate in a 2-step condensation, condenser are operated at a cooling medium temperature of +2° C and -85° C subsequently.

The ambient conditions in the flue gas are given in Table 3-1.

Table 3-1: Sampling conditions

Flue gas temperature	^{o}C	50 +/- 1
Flue gas velocity in stack	m/s	8.3
Water concentration	vol-%	11[*]

*Measured during long term test. Theoretical saturation at 50˚C 11.7 % by vol.

A gas velocity in the sampling point of 8.3 m/s requires 14.1 L/min to be extracted though a 6 mm sampling nozzle in order to achieve isokinetic sampling conditions. The necessary flow is within the operational interval of a Drechsler wash bottle with frit[5] and impingers[6,7] (operational range 10 - 30 L/min), thus no splitting of the gas flow was necessary prior to impinger or wash bottle train. Traditionally, wash bottles are utilized for applications were the sampling of highly volatile gases is emphasized while impingers are used when the gas stream contains particles[5]. It is not well documented which of the two systems is superior with respect to mass transfer between gas and liquid phase. However, for standard impinger bottles operated at design throughput (30 L/min in German and 28.3 L/min in American literature) a high collection efficiency for <u>particles</u> with a diameter of $d_p \geq 1 \mu m$ is mentioned[5,7], this is not necessarily transferable to liquid aerosols. Further the efficiency of an impinger is highly dependent on the operation point, considerable reduction in flow will also increase the particle cut size since the impact of an aerosol particle is influenced. The efficiency with respect to aerosol knock out as a function of velocity is not well documented.

3.2.2 ISOK4

The ISOK4 is a transportable multipurpose sampling system (TSP) for extraction of gas. The system is in compliance with EN, DIN, VDI, EPA, BS and ISO guidelines; specifically: EN 13284[8], VDI 2066[9] and VDI 3868[10].

The sampling system consists of a 1.5 m long cooled probe and is flexible with the choice of absorptions units, supplier of the system is Environnement S.A. Germany[11]. The principle flowsheet for sampling through a water-cooled probe and cooled gas washing bottles with frits positioned in an ice bath is shown in Figure 3-1. Note that the first gas washing bottle of the train is empty, thus functioning as a condensate collection vessel.

1: Pitot tube
2: Pressure sensor
3: Temperature sensor
4: Nozzle
5: Suction tube
6: Liquid absorbent impinger train
8: Dryer
9: Gas pump
10: Flow meter
11: Gas meter

Figure 3-1: Set-up for manual extraction and iso-kinetic sampling using the multipurpose system (TSP)

3.2.3 Impinger train

Figure 3-2 shows the impinger train setup. Note that there is no cooling of the sampled gas prior to the first impinger with 0.1 N H_2SO_4.

1: Pitot tube
2: Pressure sensor
3: Temperature sensor
4: Nozzle
5: Short suction tube
6: Impinger bottles (0.1 N H_2SO_4) on ice
7: Backup filter
8: Dryer
9: Gas pump
10: Flow meter
11: Gas meter

Figure 3-2: Setup for manual extraction and iso-kinetic sampling of gas samples using an impinger train setup.

3.2.4 Collection of condensate, "Cold trap"

For the cold trap sampling an in-house designed water cooled probe with 5 mm nozzle was utilized. A setup of two consecutive glass gas-coolers with liquid collection vessels was applied for the collection of condensate. The condensers were cooled by means of a cryostat circulating

coolant in order to achieve gas temperatures of +2°C and -85°C in the exiting gas of the first and second step, respectively. Figure 3-3 shows the described setup for condensate collection.

1: Pitot tube
2: Pressure sensor
3: Temperature sensor
4: Nozzle
5: Short cooled suction tube
6: Condenser (gas exiting T=+2°C)
7: Condenser (gas exiting T=-85°C)
8: Dryer
9: Gas pump
10: Flow meter
11: Gas meter

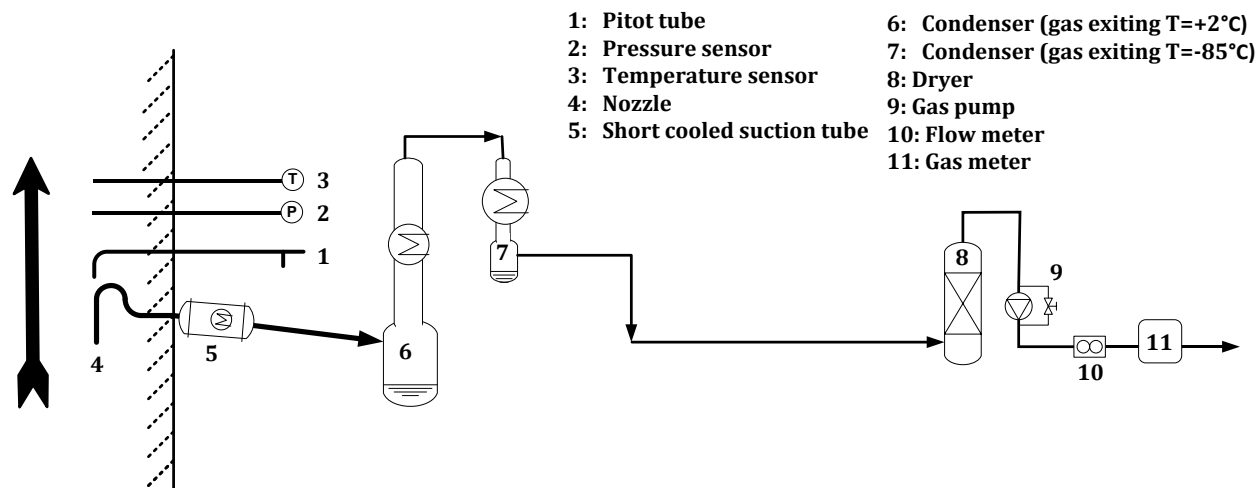**Figure 3-3: Setup for manual extraction and iso-kinetic sampling of gas samples using two subsequent gas coolers for condensate collection at +2°C and then -85°C.**

3.2.5 Results from sampling

The above described sampling devices were applied in parallel for sampling on the VOCC-rig at SINTEF, Trondheim. The results from sampling are presented in Table 3-2.

The results of the three sampling devices are rather similar in magnitude. Comparing the three set-ups, the difference is in principle in the efficiency of the first accumulation step. For ISOK4 a cooled probe and an empty gas absorption bottle without diffuser, for the impinger train app. 50 mL of liquid in the first stage and for the cold trap a high efficient gas cooler. However, considering the experiment performed with ISOK4, combining the empty first bottle (relatively low heat transfer efficiency in an empty bottle) with the second wash bottle filled with absorption liquid give similar or better efficiency compared to the other two sampling set-up's. For compounds with low boiling points, the cold trap system shows that the majority of compounds are accumulated in the first condenser (coolant temperature $+2^oC$). The classic absorption system (denoted impinger train in Table 3-2) show similar or lower efficiency compared to the condensate based systems.

Table 3-2: Concentrations of nitrosamines (NDMA and NDELA), amines (piperazine, MEA and AMP), ammonia and alkylamines (methylamine, ethylamine, dimethylamine and diethylamine) in flue gas sampled with three different sampling systems during VOCC experiment.

SAMPLE ID	NDMA		NDELA		Piperazine		MEA		AMP		NH₃		Methylamine		Ethylamine		Dimethylamine		Diethylamine	
Unit	µg/Nm³		µg/Nm³		µg/Nm³		µg/Nm³		µg/Nm³		mg /Nm³		µg/Nm³		µg/Nm³		µg/Nm³		µg/Nm³	
ISO K4 - 1.Condensation step (empty gas absorption bottle without diffuser on water/dry ice)	41,2	80 %	None		93,04	93 %	317	90 %	901,2	92 %	8	52 %	35,144	90 %	45,8	92 %	48,594	92 %	70,781	93 %
ISO K4 - 1.Absorption (Gas washing bottle) - 0.1 N H2SO4	9,69	19 %	None		5,319	5 %	32,6	9 %	78,25	8 %	7,43	48 %	2,92	7 %	3,9	8 %	3,49	7 %	5,44	7 %
ISO K4 - 2.Absorption (Gas washing bottle) - 0.1 N H2SO4	0,64	1 %	None		1,189	1 %	4,07	1 %	1,64	0 %	ND		1	3 %	ND		0,57	1 %	0,188	0 %
ISO K4 - 3. Absorption (Gas washing bottle) - empty	No liquid collected																			
SUM	51,53				99,548		353,67		981,09		15,43		39,064		49,7		52,654		76,409	
Combined contents of empty bottle plus first bottle																				
ISO K4 - 1.Condensation step	41,2		None		93,04		317		901,2		8		35,144		45,8		48,594		70,781	
ISO K4 - 1.Absorption bottle 0.1 N H2SO4	9,69	99 %	None		5,319	99 %	32,6	99 %	78,25	100 %	7,43	100 %	2,92	97 %	3,9	100 %	3,49	99 %	5,44	100 %
ISO K4 - 2.Absorption bottle 0.1 N H2SO4	0,64	1 %	None		1,189	1 %	4,07	1 %	1,64	0 %	ND		1	3 %	ND		0,57	1 %	0,188	0 %
ISO K4 - 3. Absorption empty	No liquid collected																			
SUM	51,53				99,548		353,67		981,09		15,43		39,064		49,7		52,654		76,409	
Impinger train, 1.Impinger - 0.1 N H2SO4	39,2	75 %	None		126,6	97 %	333	93 %	1052	96 %	15,67	97 %	42,52	94 %	54,7	93 %	59,23	94 %	85,85	95 %
Impinger train, 2.Impinger - 0.1 N H2SO4	13,3	25 %	None		4,24	3 %	23,6	7 %	48,31	4 %	0,419	3 %	2,869	6 %	3,82	7 %	3,81	6 %	4,208	5 %
Impinger train, 3.Impinger – empty								No liquid collected												
SUM	52,5				130,84		356,6		1100,31		16,089		45,389		58,52		63,04		90,058	
Cold-trap, condenser 1: + 2 C	39,5	97 %	None		147,8	97 %	452	99 %	1148	98 %	10,08	99 %	43,509	100 %	53,3	99 %	59,19	99 %	79,24	98 %
Cold-trap, condenser 2: -85 C	1,35	3 %	None		4,459	3 %	6,59	1 %	24,58	2 %	0,139	1 %	0,151	0 %	0,4	1 %	0,481	1 %	1,366	2 %
SUM	40,85				152,259		458,59		1172,58		10,219		43,66		53,7		59,671		80,606	

3.2.6 Esbjerg Campaign

In the Esbjerg campaign, three sampling systems were used. Two of the sampling systems (the ISOK4 and the Cold trap) were used identically to the VOCC experiment, except that the gas wash bottles of the ISOK4 system were replaced by impingers in the Esbjerg campaign. In addition, a system consisting of a heated probe with downstream splitting of the gas stream into three parallel sampling trains plus make-up train was utilized (the first gas wash bottle for condensation was always empty at start, the two following wash bottles were filled with various liquid absorbents) (System provided and operated by MOLAB). This configuration (see Figure 3-4) made it possible to perform parallel sampling with different absorption solutions simultaneously, allowing higher number of experiments could be performed in parallel (see Figure 3-4).
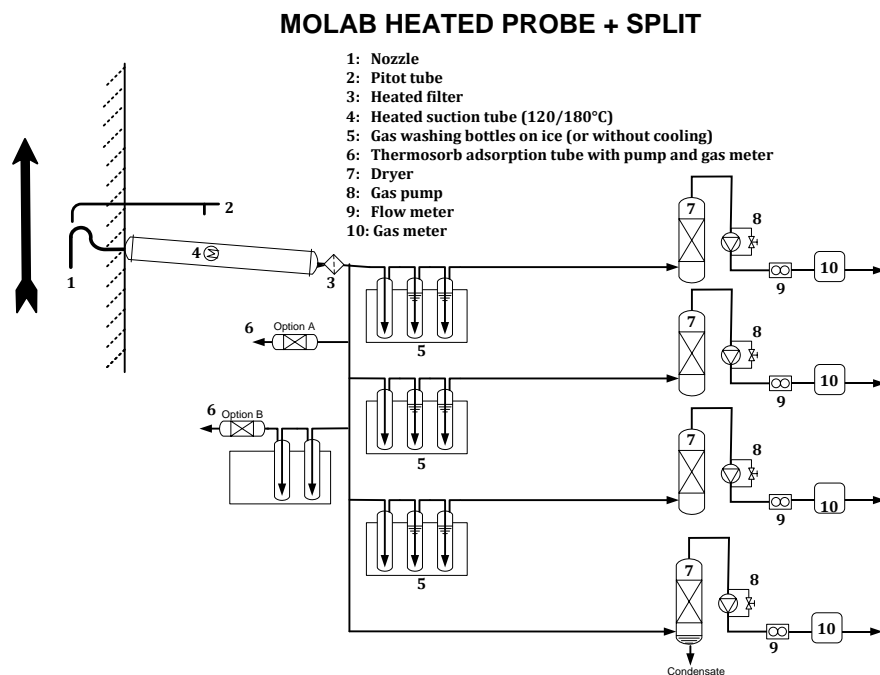
MOLAB HEATED PROBE + SPLIT

1: Nozzle
2: Pitot tube
3: Heated filter
4: Heated suction tube (120/180°C)
5: Gas washing bottles on ice (or without cooling)
6: Thermosorb adsorption tube with pump and gas meter
7: Dryer
8: Gas pump
9: Flow meter
10: Gas meter

Figure 3-4: Iso-kinetical sampling with heated probe and subsequent split of gas stream into four parallel trains (MOLAB)

The main objective for the Esbjerg Campaign was to serve as a basis for further testing of the different sampling systems described above, further generate relevant sample types for the study of sample integrity and update of sample workup and analytical procedures.

The following subgoals of the Esbjerg Campaign were:
   a) comparison of sampling efficiency of condensers vs. liquid absorption systems when the condenser was placed first in a sampling train,

b) comparison of different methods for flue gas conditioning (cooling / condensing) as integral part of the sampling (ISOK4, MOLAB and SINTEF Cold Trap),

c) comparison of different sampling solutions (0.1 M sulfamic acid, 0.1 N sulfuric acid, phosphate/citrate buffer (100 mM) with 25 mM ascorbic acid and water),

d) comparison of different temperatures in the absorption units during sampling (with and without ice) and

e) comparison of different sampling probe temperatures $120^{\circ}C$ and $180^{\circ}C$).

In addition, *nitrosation* in the condensate samples was studied by systematic addition of DEA (precursor for NDELA) and methyl-butyl amine (MBA, precursor for N-methyl-butyl nitrosamine). Methyl-butyl amine was added as a potential candidate as nitrosation marker. Sulfamic acid was added as nitrite scavenger and ascorbic acid was added as an antioxidant to prevent nitrosation of the two secondary amines.

The findings from the Esbjerg measurement campaign are summarized as follows:

a) *Comparison of sampling efficiency of condensers vs. liquid absorption systems when the condenser was placed first in a sampling train*

Example results for methylamine and ammonia are presented in Figures 3-5 and 3-6. The results show that for the volatile compound methylamine, 80 to 90% of the compound is collected by the cooled probe and cooled first wash bottle with the ISOK4 set-up (note this one was empty at beginning of the sampling).
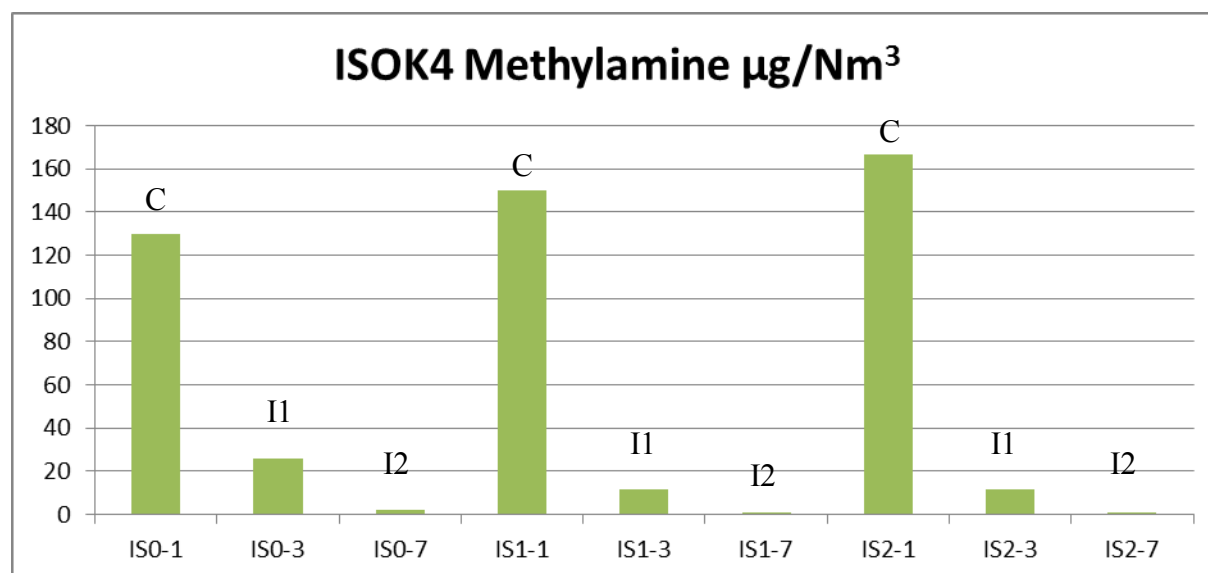

Figure 3-5: Sampling of of methylamine by the ISO K4-system. (C = condensate, I1 = impinger 1, I2 = impinger 2).

The results from ISOK4 are in accordance with the MOLAB experiments, where an average of 94% of the methylamine was captured in the first condensation bottle (n=6 trains). The results are also in accordance with the VOCC experiment where 90% of the methylamine was found in the condenser in the ISOK4 experiments.

The results for ammonia (NH_3) show that a system consisting of a cooled probe and liquid collection vessel is not sufficient since the boiling point of NH_3 (-33°C @ 1 bar(a)) is considerable lower than the operation temperature of the sampling equipment. Based on this result, it is recommended to sample ammonia in a classic liquid absorption system with 0.1 N H_2SO_4 as adsorption solution
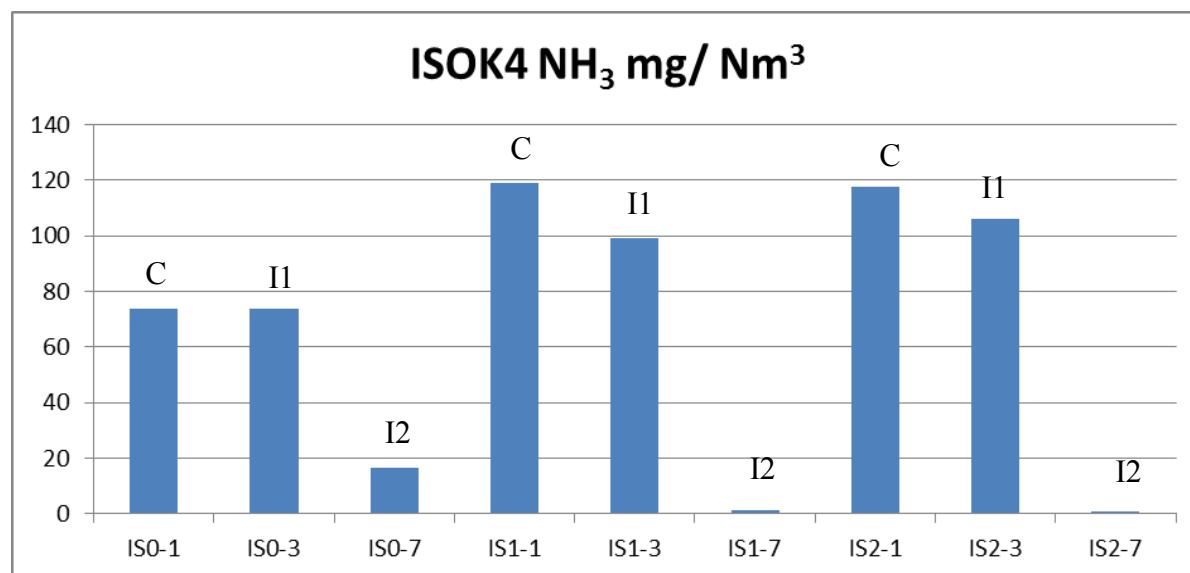

Figure 3-6: Sampling of NH_3 by the ISOK4-system. (C = condensate, I1 = impinger 1, I2 = impinger 2).

b) *Comparison of different flue gas conditioning systems (ISOK4, MOLAB and SINTEF Cold Trap)*

The calculated average amounts of methylamine from different condensers are shown in Figure 3-7 below. The result shows that different condensers seem to capture comparable amounts of methylamine, although a tendency is seen that the SINTEF Cold Trap has a better trapping efficiency than the ISOK4 and MOLAB condensers. The Cold trap was also found to have a better trapping efficiency for methylamine than the ISOK4 in the VOCC experiment. In the VOCC experiment, the trapped amounts of methylamine were comparable with a classic liquid absorption train with 0.1 N H_2SO_4. However, in the VOCC experiment the Cold Trap collected

more of the solvent amines than the other two systems (Table 3-2). The higher efficiency of the cold trap is achieved because of a higher residence time of the flue gas in the condenser and design optimization for condensation compared to the non-optimum design of an empty gas wash bottle with its limited residence time and heat transfer capability.
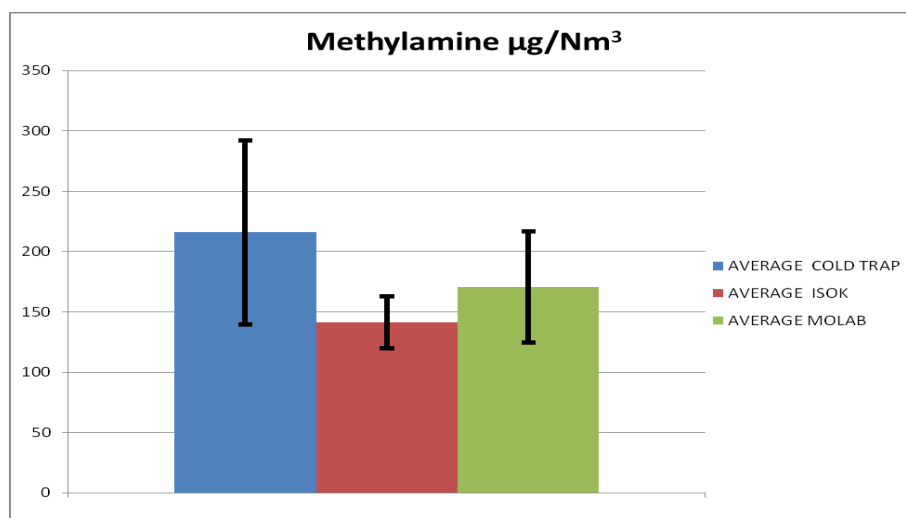

Figure 3-7: Measurement of methylamine with ISOK4, MOLAB and SINTEF Cold Trap in the Esbjerg Campaign given as average +/- standard deviation. (ISOK4 n=4, MOLAB n=16 and SINTEF Cold Trap n= 7)

c) *Comparison of different sampling solutions (0.1 M sulfamic acid, 0.1 N sulfuric acid phosphate/citrate buffer (100 mM) with 25 mM ascorbic acid and water)*
Due to the fact that all experiments with absorption solutions were performed with the absorption solutions in a train downstream to the condenser, it is difficult to compare these. From the MOLAB data, it can be seen, however, that the solutions of sulfuric acid, sulfamic acid, phosphate citrate buffer and water are comparable with respect to trapping of methylamine.

d) *Different temperatures in the absorption units during sampling (with and without ice)*
Only three experiments in the MOLAB series were performed without ice in the absorber units. The data from these experiments do not clearly indicate that less methylamine is captured without ice, neither in the condensers nor in the absorption solutions.

e) *Different sampling probe temperatures ($120^{o}C$ and $180^{o}C$)*
Two experiments were performed at 180˚C in the MOLAB series. Compared to the results at $120^{o}C$, no difference was indicated for methylamine in the experiments with the $180^{o}C$ probe.

3.2.7 Nitrosation experiments

The nitrosation experiments were performed in condensate samples from the SINTEF Cold Trap condenser. In these experiments, condensate was spiked with 1) SA alone, 2) DEA + MBA, 3) SA + DEA + MBA, 4) AA alone, 5) AA + DEA + MBA and finally 6) SA + AA + DEA + MBA.

The experiment was designed to find out if native DEA in the sample (or DEA added to the sample) could be nitrosated (by native nitrite in the condensate sample) during storage. Furthermore, it was also important to find out if the addition of SA or AA (or both) could prevent the nitrosation. MBA was added as a possible nitrosation marker which could be expected to be nitrosated to the corresponding nitrosamine N-methyl-butyl nitrosamine.

The result from this experiment revealed that no formation of nitrosamine could be detected in any experiment, either without or with SA or AA. (the detection limit for NDELA was < 1 ug/L in these measurements). This observation strongly indicates that nitrosation did not occur in condensate. The observation is supported by the results of NO_2 measurements in the condensate samples performed by Statoil (Porsgrunn). These measurements indicated very low concentrations of NO_2 in the condensates (between 39 and 108 ug/L in untreated condensate). Condensate sample added SA as NO_2 scavenger, had concentrations of NO_2 below 10 ug/L. This shows that SA has an effect as scavenger when added to the condensate sample.

3.3 Summary sampling methodology (capture of analyte)

The procedures for sampling are given in the procedures attached as appendices of this report. The organization of the procedures is based on, and are in accordance with ISO 11338.

The present procedure for isokinetic sampling of flue gas is based on a) a cooled probe, followed by b) a high efficiency gas cooler (condenser) followed by c) an absorption train consisting of at least three gas wash bottles in series. The methodology allows the use of a solid adsorbent unit (Ø50X90mm) downstream to the condensate trap and the gas wash bottles acting as a safety device or "police filter". Please note that the classical miniaturized activated carbon filled tubes (Ø8x100mm) are not applicable for this application, both with respect to humidity in the flue gas which will clog the adsorption surface and the gas flow necessary for isokinetical sampling.

The combined cooled probe – condenser incl. liquid collection vessel – liquid absorption system (see Figure 3-8) has the following characteristics:

1)   Cooled probe to prevent artefacts; operated to ensure isokinetical sampling

2) Fast sampling gives short residence time for analytes in condenser (prevent artefacts)

3) Short sampling times for condensate allows multiple consecutive samplings

4) Easy collection of condensate aliquots for further treatment (additives)

5) Easy collection of condensate aliquots for immediate storage

6) The condensate water is a very clean sample matrix free of additives often used in absorption solutions for liquid absorption sampling

7) The system is commercially available both as components and automated system

The system presented in Figure 3-8 is additionally equipped with liquid absorption units (standard liquid wash bottles; three liquid filled, one empty to avoid droplet carry over) and solid adsorbent unit. Combination of three collection steps allow for efficient sampling of compounds. An overview of the chemicals used in the individual stages of the sampling units is given in Table 3-3; engineering details are compiled in Table 3-4. The characteristics of the system listed above are discussed further in section 4.1.

1: Nozzle
2: Cooled suction tube
3: Condenser
5: Absorption units
6: Solid adsorption unit
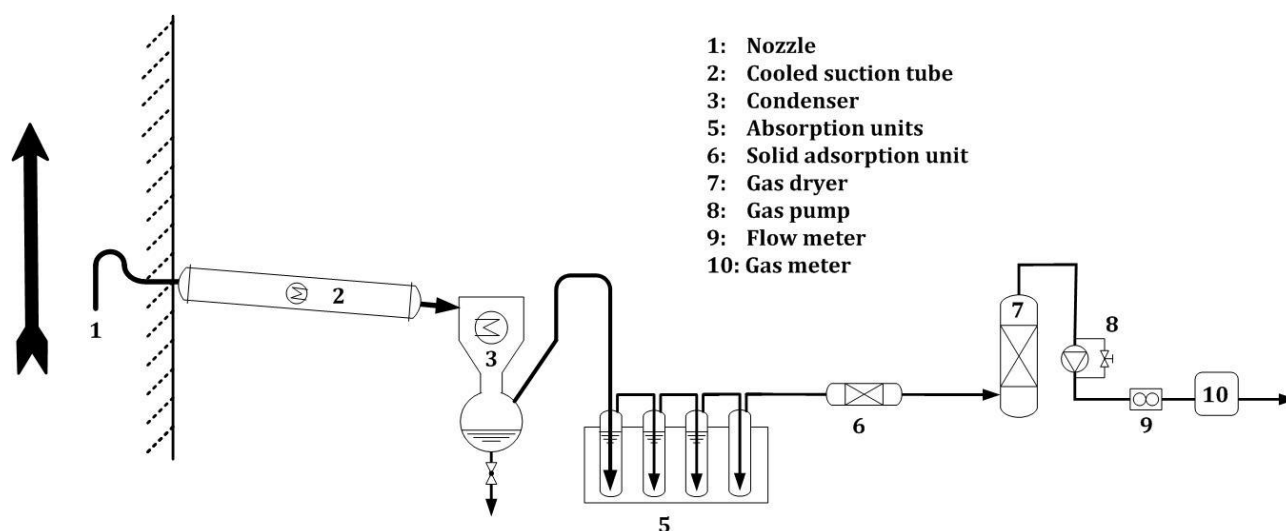7: Gas dryer
8: Gas pump
9: Flow meter
10: Gas meter

Figure 3-8: Set-up for manual iso-kinetic sampling using the multipurpose system (TSP), extension with high efficiency gas cooler

Table 3-3: Overview chemicals used in sampling train

Component group	Sampling train sequence	Description and specifications				
		Condensation	Liquid Absorption		Solid adsorbent	Comments
itrosamines	See Table 3-4	Yes	0.1 M Sulphamic acid	100 ml, aqueous solution	Ø50x90mm	Sampling train based on EN 11338, modified with condenser, condensate collection and microfilter to handle high humidity and mist in flue gas. Details see chapter 4.2
Total Nitrosamines		Yes	0.1 M Sulphamic acid	100 ml, aqueous solution	Ø50x90mm	
Nitramines		Yes	0.1 M Sulphamic acid	100 ml, aqueous solution	Ø50x90mm	
Solvent amines		Yes	0.1 M Sulphamic acid	100 ml, aqueous solution	Ø50x90mm	
Alkylamines		Yes	0.1 M Sulphamic acid	100 ml, aqueous solution	Ø50x90mm	
Aldehydes		Yes	0.1 M Sulphamic acid	100 ml, aqueous solution	Ø50x90mm	
Ammonia	Impinger train	No	0.1 N H2SO4	100 ml, aqueous solution		VDI 3496; 1982

Table 3-4: Sampling train sequence overview

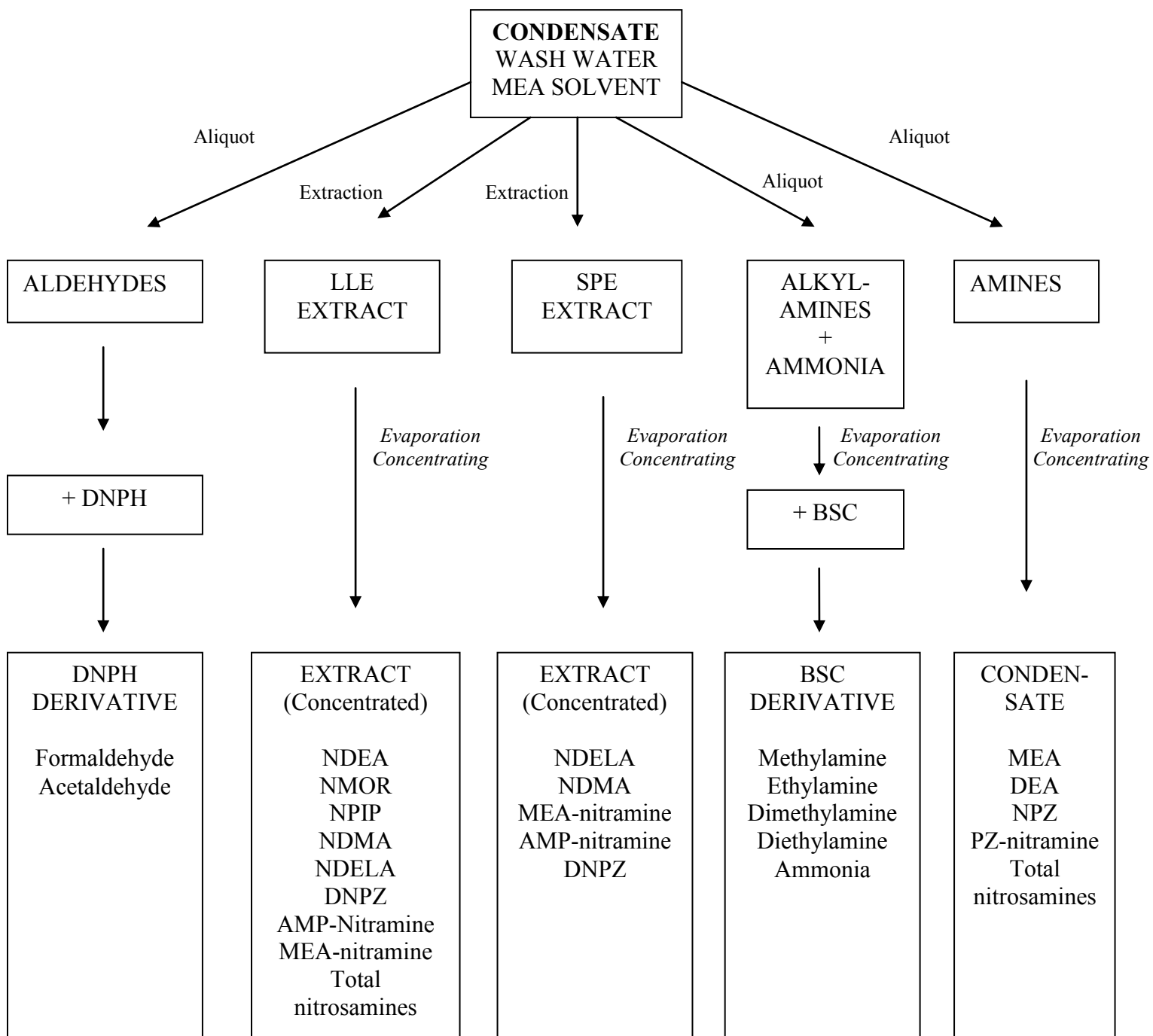|	Nozzle	Cooled sampling probe	Condenser	Collection flask	Absorption units	Solid adsorption units	Gas cooler	Gas dryer	Gas pump, flow meter and gas meter	Control unit: Isokinetical sampling and operation data recording
Sampling train sequence	Size needs to be adjusted to ensure isokinetical sampling and proper operation of sampling train. Strongly dependent on choice of liquid absorption units (wash bottle and standard impinger 10 - 30 l/min). For operation with mist: 30 l/min	Cooled sampling probe, length dependent on stack design. Type: Cooled Combination Suction Tube; Version B with S-pitot tube and thermocouple	Spiral condenser, length 500 mm NS29/32 cone and socket	Cooled Condensate Collection vessel 2 l with GL45 thread. With impinger tube and glass angles to connect the absorption-systems.	Gas wash bottle with frit 0, 250 l volume, Entrance Pan KS19, Exit Ball KS 19. Minimum three bottles, sequence two liquid filled, one empty to avoid droplet carryover, advised one empty in front of first filled to avoid droplet entrainment.	Adsorption trap, filled with XAD 2, trap dimension ID Ø = 50 mm, length minimum 90 mm http://www.paulgothe.de/english/inhalt/dioxin_2007.pdf	Large gas cooler with water separator: Cooling device: Ø 220 x 200 mm, approx. 3 m of cooling coil (tube 18 x 1.5 mm) with handle. Integrated water condensate trap for 7 litre with inspection glass, discharge cock, and gas connector, weight approx. 9,8 kg , size: 350 x 350 x 590 mm	Big drying tower. Material: PVC-tube, Ø 160 x 400 mm, with two threads in the cover. Dry Volume: Ø 150 x 300 mm (~ 5,3 l / ~ 4,3 kg silica-gel 1060 g H_2O-adsorption)	Gas sampler with rotary pump, capacity 2.4 m3/h, including flowmeter, thermometer vaccum gauge	Automatic Isokinetic Sampler ITES or ISOK4
Supplier		Supplier: Paul Gothe Messtechnik or Environnement SA	http://www.lenz-laborglas.de	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik
Chemicals			N/A	N/A	See ????????	XAD-2		Silica Gel, 4.3 kg		
Comments:					Analysis of these samples require consideration with respect to necessity. Provided >90% of the analytes are present in the condensate, the necessity of analysis of the absorption liquids needs to be considered.	Police filter similar consideration as for a liquid absorption solution is necessary				

3.4 Sample preparation procedure

The procedures for sample preparation are given in the procedures attached as appendices of this report. The procedures describe all steps of sample preparation including liquid-liquid extraction (LLE) and solid phase extraction (SPE) for samples of condensate, impinger solutions, wash water and MEA solvent. An overall process flow sheet for the extraction procedures and concentrating is given in Figure 3-6 below.

The most important purpose with the LLE and the SPE extractions is the *removal of MEA* solvent amine prior to the instrumental analysis of trace analytes (e.g. nitrosamines and nitramines) with LC-MS. The reason for this is that amine solvents are dominating compounds in samples from wash water and flue gas, in concentrations up to six orders of magnitude (10^6) higher than the trace analytes. Such high relative concentrations of solvent amine cause interferences with the instrumental analysis of the trace analytes.

It should also be noted that the LLE and SPE procedures alone (i.e. without evaporation) makes it possible to inject the sample *undiluted* due to the lowered concentration of MEA in cases where this not was possible previously (wash water and MEA solvent).

One other very important purpose of the LLE and SPE extractions is to increase the analytical sensitivity by *concentrating the extract by evaporation.*

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FIGURE 3-6:OVERALL PROCESS FLOW SHEET

```
                           ┌─────────────────┐
                           │   CONDENSATE    │
                           │  WASH WATER     │
                           │  MEA SOLVENT    │
                           └─────────────────┘
```

Aliquot · Extraction · Extraction · Aliquot · Aliquot

ALDEHYDES	LLE EXTRACT	SPE EXTRACT	ALKYL-AMINES + AMMONIA	AMINES

Evaporation Concentrating (LLE) · *Evaporation Concentrating* (SPE) · *Evaporation Concentrating* (ALKYL-AMINES) · *Evaporation Concentrating* (AMINES)

+ DNPH			+ BSC	

DNPH DERIVATIVE	EXTRACT (Concentrated)	EXTRACT (Concentrated)	BSC DERIVATIVE	CONDEN-SATE
Formaldehyde Acetaldehyde	NDEA NMOR NPIP NDMA NDELA DNPZ AMP-Nitramine MEA-nitramine Total nitrosamines	NDELA NDMA MEA-nitramine AMP-nitramine DNPZ	Methylamine Ethylamine Dimethylamine Diethylamine Ammonia	MEA DEA NPZ PZ-nitramine Total nitrosamines

3.5 Analysis (instrumental analysis)

The procedures for instrumental analysis are given in the procedures attached as appendices of this report. The procedures are given for single analytes and for groups of analytes (nitrosamines, nitramines and alkylamines).

The analytical methods are based on *mass spectrometry*, which provides high *specificity* and high instrumental *sensitivity*. The nitrosamines (NDMA, NDEA, NMOR, NPIP, NDELA, NPZ and DNPZ) the nitramines (MEA-nitramine, AMP-nitramine and piperazine nitramine), the amines (MEA, DEA, AMP and piperazine) and the aldehydes (formaldehyde and acetaldehyde) are analysed with liquid chromatography and (triplequadrupole) mass spectrometry (LC-MS-MS-QQQ). The alkylamines (methylamine, ethylamine, dimethylamine and diethylamine) and ammonia are analysed with gas chromatography – mass spectrometry (GC-MS). Total nitrosamine is analyzed by gas chromatography and nitrogen chemiluminescence detection (GC-MS-NCD).

3.6 Analytical sensitivity for the combined methodologies

In section 7, an overview of the analytical sensitivities for the combined methodologies is given. The sensitivities are given for flue gas condensate, extracts of flue gas condensate (Table 7-1), wash water (Table 7-2) and MEA solvent (Table 7-3).

For *condensate* and *wash water*, a general increase in sensitivity by a factor of 10-50X has been achieved. This is the effect of clean-up by LLE and the possibility of direct injections *and* concentrating of the extracts. This effect is largest for wash water, which may have an amine concentration of several hundred millimoles/L. A further optimization by increasing the concentrating by evaporation is possible.

For measurements in amine (MEA) *solvent*, a general increase in sensitivity by a factor of at least 100X has been achieved. This factor is the result of the possibility of injecting of the extract from LLE (and SPE) clean-up of solvent directly without dilution to the LC-MS-MS-QQQ system. An optimization by further evaporation is possible also here.

4 Discussion

4.1 Sampling methodology (capture of analyte)

The sampling system described in the procedures in the appendices utilizes a *cooled probe and condenser* as the main principle for capture of analyte. The rationale behind this is that polar and water soluble compounds will follow water during a condensation process, this was early observed for the volatile nitrosamine NDMA when a condenser was placed in front of an adsorption tube to remove water. Later, in H&E TQP ID 1, calloff 1[4] it was demonstrated in experiments (the VOCC experiments) that the nitrosamine NDMA, the most volatile alkylamines (methylamine, ethylamine, dimethylamine and diethylamine) and the solvent amines (MEA, AMP and piperazine) *all* were trapped efficiently both in simple condensation flasks and in a condenser dedicated for the purpose of efficient gas cooling. In the VOCC experiments, three different sampling systems were tested, the ISOK4 system with gas wash bottles with frit, a "classic" impinger train with 0.1 N H_2SO_4 and a simple two-stage cold trap (+2ºC and - 85ºC). The results in all three systems were remarkably consistent, which indicated that the concept of trapping analytes in a condenser is functional (see Table 3-2). In the present project, H&E TQP ID 1 calloff 2, the results from the Esbjerg sampling campaign confirms the efficiency of the condensation arrangement.

In one of the Esbjerg experiments (ISOK4) sampling was performed with a very high flue gas velocity (14 m/s) through the probe, a lowered trapping efficiency was observed for MEA with a considerable transfer of MEA to the first gas wash bottle with absorption solution. Surprisingly, this was not observed the alkylamines in the same sampling. This observation is interesting as it indicates that compounds with different volatility may behave differently in the condenser. However, 14 m/s is an extreme velocity that gives a very short contact time with the walls of the cooled probe and also insufficient cooling of the flue gas in the first empty flask. At moderate velocities through the condenser flasks, of <5 m/s (as tested in a parallel MOLAB experiment) a 99% trapping efficiency (compared to gas wash bottle 1) was found for MEA. The ISO K4 experiment revealed that if the first conditioning step (here a condenser) is poorly designed / operated a second stage trap, in some cases, may be important for control and verification of the trapping efficiency.

As stated in section 3.3 (points 1 through 7), there are some important characteristics and advantages that are specific for the combined cooled probe – condenser – liquid absorption system. These characteristics and advantages are discussed below.

Isokinetic sampling is regarded as mandatory as described in TQP ID 1, subtask 1, calloff 1. The presented system allows *isokinetic sampling* in one single stream through all parts of the system or if necessary, with a split to two (or more) absorption trains after the condenser. An optional separate sidestream for adjustment of the total flue gas stream to keep isokinetic velocity at the probe nozzle is easily facilitated.

The system has a *cooled probe*. The reason for this is that probes with elevated temperatures may cause artefacts that will cause erroneous results for some analytes. It has been found that heated probes (with FT-IR) have caused *thermal decomposition* at temperatures as low as 120°C[12]. At 180°C[13], a probe / transfer line temperature commonly used by on-line measurements, the risk for thermal decomposition is very high for many analytes[2,3]. In the TQP ID 1 study, a strong focus has been directed towards *nitrosation*, i.e. the formation of nitrosamines from the reaction between secondary amines and nitrogen oxides like NO_2. It is anticipated that elevated temperature will increase the risk of nitrosation to occur.

Compared to liquid absorption sampling, an efficient condenser will give *fast production of condensate that has a representative concentration* from the first drop of condensate, and there is no need to build up a concentration from a zero-concentration starting volume (100 mL, typically) of absorbent solution in absorption medium. This makes it possible to operate with a *short residence time in the condenser* which will reduce the risk for artefacts. If large samples not are needed, for sensitivity reasons, it will be possible to perform *multiple consecutive samplings*. This may be relevant for the study of transient or immediate effects on emissions from changes in operational parameters of the amine plant.

Condensate can be easily collected from the liquid collection vessel below the condenser by a stop-cock in the bottom of the trap. This makes it possible take aliquots for specific analyses that requires *specific sample treatment* (like addition of the derivatization agent DNPH for analysis of aldehydes) or the need for *specific additives* like anti-nitrosating agents (e.g. sulfamic acid), for preservation (although a need for anti-nitrosating agent not was indicated by the Esbjerg nitrosation experiment), or the addition of nitrosation markers (like the secondary amine methyl-butyl amine) or the addition of a deuterated internal standard to secure the total process line of sample preparation and handling.

The fast production and easy collection of condensate makes fast transfer to *immediate storage* and preservation at lowered temperature (freezer at -20°C) for long term storage possible.

It should be emphasized that condensate as a sample matrix represent a *very clean sample matrix* without the presence of strong concentrations of acids like 0.1 N H_2SO_4 or 0.1 M sulfamic acid when these are used as liquid absorption solutions.

Finally, it should be registered that all parts of the combined cooled probe – condenser – impinger or gas wash bottles system are *commercially available* as standardized glassware and as whole integrated sampling systems (like the ISOK4 automated sampling system).

The impinger / wash bottles of the sampling system are mainly *a second-line control of sampling efficiency*. However, the impingers / wash bottles seem to be needed for accurate 100% sampling of ammonia. Provided ammonia is the main target of a sampling campaign, a simpler absorber train without condenser would probably be a better and simpler alternative. Sampling of ammonia from flue gas has been performed in 0.1 N H_2SO_4 absorber trains historically[14] and standards have been established for this.

The utilization of solid adsorbents (e.g.: XAD-2 downstream to the condenser and liquid filled absorbers) is possible to ensure that all organic compounds can be sampled. However, the results presented show that the concentration of some key compounds in the second unit of an absorber train is below detection limit for the chosen analytical technologies. Therefore; provided proper design of the up-stream units as discussed previously; the XAD-2 adsorbent has solely a control function (police filter).

In conclusion, the combined cold probe – condenser – liquid absorber system represents an integrated sampling system that has several advantages compared to classic liquid absorber (impinger)-only systems. For the purposes given in the scope of this project, this system is suggested and recommended for the integrated sampling of the analytes given in the scope.

4.2 Sampling from flue gas streams with high content of aerosols

Sampling in gas streams containing a high concentration of aerosols has only recently been discussed as part of the project and is therefore only considered in the discussion since an experimental verification could not be performed because of the prevailing framework of the contract.

Sampling of aerosols (liquid and particles) of less than 1 μm is challenging since there is only limited knowledge regarding the behaviour of aerosols in standard sampling equipment. Experiments performed at Esbjerg indicate some inconsistency between sampling systems which

are not fully understood. One possible explanation is that aerosols are not sufficiently well trapped in the systems (Note: a standard impinger is designed for $d_p \geq 1\mu m$ @ 30 l/min) since deviation from the design operation point will increase the cut size. Similar discussions are on-going with respect to manual sampling of dioxins and furans. In these systems adsorption cartridges of approximately Ø50x300 mm filled with quartz wool and XAD-2 resin particles are utilized. Considerable concern[15] has been risen how efficient these systems are for aerosols of $d_p \leq 1\mu m$; therefore development is performed to adapt sampling systems with filter units with a efficiency of 99.98% for $d_p \geq 0.1\mu m$. The relevant standards will be revised during 2012.

Considering these issues and the lately expressed concerns by Company regarding type (phase and size) of aerosols and their concentration in the flue gas a revised version of the sampling system is recommended (see Figure 4-1). The principle flowsheet is identical to the system presented in Figure 3-8 consisting of cooled probe, condenser and downstream absorption bottles. However, a *microfilter* is installed after the condensate collection vessel (see Figure 4-1). The filter is designed to efficiently (99.99%) remove droplets of 0.1μm and has been tested for flue gases from waste incineration plants for the measurement of dioxin/furan. The filter media is after performed sampling rinsed with water and acetone, the solution is then analysed. Please note, the experimental verification of the utilization of this filter in the current application (sweetening of flue gas) is pending per February 2012.

1: Nozzle
2: Cooled suction tube
3: Condenser
4: Filter
5: Absorption units
6: Solid adsorption unit
7: Gas dryer
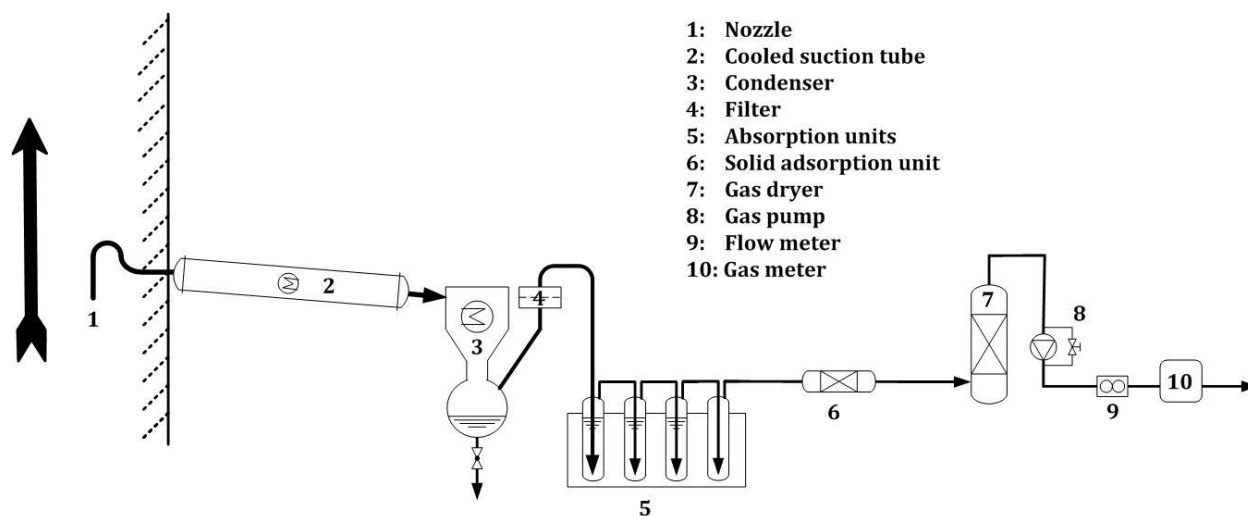8: Gas pump
9: Flow meter
10: Gas meter

Figure 4-1: Extended sampling system

An overview of the sampling set-up for gas streams with high aerosol content is given in Table 4-1.

Table 4-1: Overview over sampling system for flue gas with high aerosol content

	Nozzle	Cooled sampling probe	Condenser	Collection flask	Aerosol filter	Absorption units	Solid adsorption units	Gas cooler	Gas dryer	Gas pump, flow meter and gas meter	Control unit: Isokinetical sampling and operation data recording
Sampling train sequence	Size needs to be adjusted to ensure isokinetical sampling and proper operation of sampling train. Strongly dependent on choice of liquid absorption units (wash bottle and standard impinger 10 - 30 l/min). For operation with mist: 30 l/min	Cooled sampling probe, length dependent on stack design. Type: Cooled Combination Suction Tube; Version B with S-pitot tube and thermocouple	Spiral condenser, length 500 mm NS29/32 cone and socket	Cooled Condensate Collection vessel 2 l with GL45 thread. With impinger tube and glass angles to connect the absorption-systems.	Microglasfiber filter in PTFE housing, specification: 99.98 % recovery @ 0.1 mm. PTFE housing G1/2" connection, filter house volume 90 ml	Gas wash bottle with frit 0, 250 l volume, Entrance Pan KS19, Exit Ball KS 19. Minimum three bottles, sequence two liquid filled, one empty to avoid droplet carryover, advised one empty in front of first filled in case aerosol filter with liquid collection is omitted .	Adsorption trap, filled with XAD 2, trap dimension ID Ø = 50 mm, length minimum 90 mm http://www.paul gothe.de/english/ inhalt/dioxin_200 7.pdf	Large gas cooler with water separator: Cooling device: Ø 220 x 200 mm, approx. 3 m of cooling coil (tube 18 x 1.5 mm) with handle. Integrated water condensate trap for 7 litre with inspection glass, discharge cock, and gas connector, weight approx. 9,8 kg , size: 350 x 350 x 590 mm	Big drying tower. Material: PVC-tube, Ø 160 x 400 mm, with two threads in the cover. Dry Volume: Ø 150 x 300 mm (~ 5,3 l / ~ 4,3 kg silica-gel 1060 g H_2O-adsorption)	Gas sampler with rotary pump, capacity 2.4 m3/h, including flowmeter, thermometer vaccum gauge	Automatic Isokinetic Sampler ITES or ISOK4
Supplier		Supplier: Paul Gothe Messtechnik or Environnement SA	http://www.l enz-laborglas.de	Paul Gothe Messtechnik	Environnement SA	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik	Paul Gothe Messtechnik
Chemicals			N/A	N/A		See table above	XAD-2		Silica Gel, 4.3 kg		
Comments:				Liquid collected in microfilter and condensate collector are combined. Filter material itself is cleaned with water and aceton and analysed individually	Operation with aerosols/mist require special consideration, testing of microfilter pending per january 2012	Analysis of these samples require consideration with respect to necessity. Provided >90% of the analytes are present in the condensate and aerosol filter, the necessity of analysis of the absorption liquids needs to be considered.	Police filter similar consideration as for a liquid absorption solution is necessary				

4.3 Sample preparation (sample workup)

There are several challenges associated with sample preparation and extraction of the *very polar and water soluble* compounds listed in the scope of work *from polar aqueous samples*. For this reason, our strategy has been to *remove the interferences* from the sample rather than to remove (extract) the analytes from the sample. For this purpose, two different approaches for removal of the major interfering compound, the amine (MEA) have been developed, one LLE extraction method with the polar ethyl acetate as extraction solvent and one SPE method where Amberlite IR 120 SO_3^- (polystyrene functionalized with sulfonic acid groups) have been applied as cation exchange material for adsorption and removal of amines from the aqueous sample.

The overall process flow sheet for the extraction procedures is shown in Figure 3-6 shows in which aliquots and in which extracts the different analytes are to be analyzed. Although condensate is the main targeted sample matrix in this project, wash water and amine solvent (MEA) can be processed according to the flow sheet given.

As can be seen, the *nitrosamines* and the *nitramines* are covered by two extraction methods, LLE and SPE. The two methods are complementary to each other in the way that the SPE method works best for the most water soluble analytes (NDELA, NDMA and the nitramines), while the LLE method performs best for the less polar nitrosamines (NDEA, NPIP and NMOR). The extracts from LLE and SPE procedures can be decreased in volume by evaporation with a subsequent concentrating of the analytes. *If one single common extraction method for both nitrosamines and nitramines is aimed, the LLE extraction procedure is recommended.*

The *alkylamines* (methylamine, ethylamine, dimethylamine are diethylamine) are *basic* amines, and will consequently not be extracted by the LLE and the SPE methods. These analytes must therefore be analyzed in unextracted condensate, wash water or MEA solvent. It should be noted that for alkylamine determination, the *unextracted* condensate can be concentrated by a factor of at least 10 times before analysis by evaporation. The reason for this is that the alkylamine GC-MS method is robust to the presence of amine (MEA) in the sample.

Ammonia is determined by the same method as the alkylamines (and in the same sample). Due to the fact that ammonia is not fully absorbed in the condensate, it will be necessary to analyse ammonia also in the first impinger downstream of the condenser. The experiments indicate that ca. 50% of the ammonia in the flue gas will be captured in the condensate and another 50% will

be captured in the first liquid filled impinger. The preferred impinger solution for ammonia is 0.1 N H_2SO_4 in accordance with existing standards for measurement of ammonia in flue gases[14].

The concentrations of ammonia encountered so far in the Esbjerg campaign, indicate that concentrating prior to analysis is not needed for ammonia. However, if ammonia is the main target of a sampling campaign, a simpler impinger train without condenser would probably be a better and simpler alternative and should therefore be considered. Sampling of ammonia from flue gas has been performed in impinger trains historically, and standards have been established for this compound.

The *aldehydes* (formaldehyde and acetaldehyde) are trapped in the condensation trap of the system. The Esbjerg samplings indicate that the aldehydes are present in flue gas concentrations that are high compared to the detection limits of the instrumental method. Therefore, no attempts have been made to concentrate the aldehydes by evaporation, so far.

It should be noted that the maximum concentrating factor that has been applied to condensate and wash water with the LLE extract and reported with results in this work is 100X. Concentrating extracts further by volume to 500X would represent no problem. The sample preparation methodologies presented thus have a considerable potential for further optimization with respect to process design and selection of extraction media and concentrating procedure.

In conclusion, the suggested overall procedure for sample preparation covers the analytes given in the scope of work. Although the main target matrix in this study is flue gas, the procedures given for sample preparation also is valid for wash water and MEA solvent. Two complementary extraction procedures based on liquid-liquid-extraction (LLE) and solid phase extraction (SPE) are given as central parts of the procedure. If one single common extraction method for both nitrosamines and nitramines is aimed, the LLE extraction procedure is recommended. The sample preparation methodologies presented have potential for further optimization.

4.4   Analysis (instrumental analysis)

A main goal for the method development in this study has been to develop methodology that gives a *high specificity* in combination with *high sensitivity*. In addition, it has been regarded as important that the *methodology is universal and versatile* in sense of being able to analyze a high number of different compounds by use of the same methodological principle and the same instruments. Finally, it has also been important to search for methodologies which are well established within fields where the demands for *secure qualitative and accurate quantitative analysis* have been the highest, and where *standards and guidelines and criteria exist* for acceptance and quality control of an analytical result (e.g.: drugs of abuse analysis, forensic toxicology and doping/sports medicine).

The above criteria have been a basis for SINTEFs strategy for selection of method principle and development. As a result of this, we have recommended and developed *mass spectrometric* methodology for the analytes given in the scope of H&E TQP ID 1. The argumentation and documentation for this is described in the SINTEF reports from H&E TQP ID 1 subtask 4[16] and 5[4].

The instrumental methods described in appendices of this report, have been organized to cover all the required aspects demanded in the standard ISO 17025. The descriptions have been made for *single analytes*, but where practically feasible, the method descriptions have been written so that *related analytes have been grouped together*.

The method descriptions have been updated with respect to modifications and improvements with a special focus on adaptation to the sample preparation (sample work-up) procedures given in section 3.4.

All analytical methods (although mass spectrometric method to a lesser extent) have an inherent problem that compounds other than the analytes may interfere with the analytical result. Most commonly, the interfering compounds are present in the sample as dominating compounds. As result hereof, dilutions have often been necessary before instrumental analysis to avoid interference, especially from strong solutions of amine solvents like MEA itself. With the sample preparation procedures given in the appendices of this report, *most of these problems have been overcome by means of efficient removal of amine solvent (MEA)*.

It should be noted that the methods for removal of solvent amine also will result in *removal of other amines* that has a basic amine group. Two specific examples are nitrosopiperazine (NPZ) and piperazine-nitramine which has a basic amine function in addition to the nitroso- and the nitro- functional groups. These compounds should therefore be analyzed by direct injection of condensate or concentrated condensate without LLE or SPE extraction.

The same situation is valid also for alkyl amines. These are primary and secondary amines and will therefore be removed together with the solvent amines by the LLE and SPE extraction procedures. However, the analytical methodology for alkylamines is GC-MS with a derivatization procedure that makes the methodology robust and less sensitive to interference from MEA. Therefore, the alkylamines can be analyzed not only directly in condensate and wash water, but also in unextracted condensate that has been concentrated by evaporation.

No interactions have been identified for other compounds than the above mentioned NPZ, the PZ-nitramine and the alkylamines.

The instrumental methodologies presented may have a considerable potential for further optimization.

In conclusion, mass spectrometric methodology has been developed that cover the list of analytes given in the scope. The methods are based on liquid chromatography with triplequadrupole mass spectrometry (LC-MS-MS-QQQ) for nitrosamines, nitramines, amines and aldehydes, on gas chromatography with mass spectrometry (GC-MS) for the alkylamines and ammonia and on gas chromatography with nitrogen chemiluminescence (GC-MS-NCD) for total nitrosamine. The analytical methods have been adapted to the procedures for sampling (capture of analyte) and sample preparation (work-up). The instrumental methodologies have considerable potential for further optimization.

4.5   Analytical sensitivity for the combined methods

As shown in section 7, and reported in section 3.1, a considerable achievement has been made for the analytical sensitivity for the methods in this project. The achievements are the effect of two factors: 1) A better clean-up with removal of MEA prior to the instrumental analysis that makes it possible to analyze samples with a high (from 500 mM to 5 M) concentrations of MEA after the removal of MEA by extraction, and 2) The effect of concentrating of the extract by

reduction of the volume by evaporation. There is potential for further optimization of the sample preparation methodologies.

The analytical sensitivities for flue gas condensate listed in Table 7-1 will for a given flue gas volume of 1 Nm^3 and a given volume of condensate of 0.05L (relevant figures for a 1 hour sample with Esbjerg conditions) will for a compound with analytical sensitivity of 5 ng/L (corresponding to the instrumental sensitivity for NDMA and NDELA in condensate after concentrating) give an analytical sensitivity in flue gas of:

Flue gas concentration = (Concentration of analyte in extract (ng/L) x volume of extract (L)) / flue gas volume (Nm3).

Calculated sensitivity example of flue gas concentration = (5 ng/L x 0.05 L) / 1 Nm^3 = 0.25 ng/Nm^3

This value corresponds to 0.25 ng/Nm^3, after 1 hour (1 Nm3) sampling, which is considered as low (compared to the sensitivity of 100 ng/Nm^3 for the most sensitive single PAH after a 6 hours (6 Nm3) sampling, in ISO 11338).

Notice that the concentration of analyte in the condensate not will increase with increased sampling time. Only a larger volume of condensate will be produced.

In conclusion, the overall effect of the sample preparation procedure is an increased sensitivity of one to two orders of magnitude for the majority of compounds under study in this project. This extra sensitivity, will applied with flue gas samples, give an analytical sensitivity in the sub nanogram per Nm^3 range.

5 Conclusions

The *combined cold probe – condenser – liquid absorber system* represents an integrated sampling system for isokinetic sampling that has several advantages compared to a classic liquid absorber-only system (gas wash bottle with frit or impinger). For the purposes given in the initial scope of this project, this system is suggested and recommended for the integrated sampling of the analytes given in the scope. The performed experiments show that a properly designed cooled probe with a condenser and collection of the condensate, is an adequate method for sampling of amine based flue gas. The liquid absorption units are included solely as a second line of absorption.

Recent concerns regarding the share of emissions caused by aerosols of $d_p \leq 1$ μm require attention, it is therefore proposed to extend the recommended sampling system by a *microfilter* (removes droplets of $d_p \geq 0.1$μm) to reduce slip of aerosols and perform a proper experimental verification.

The suggested *overall procedure for sample preparation* covers the analytes given in the scope of work. Although the main target matrix in this study is flue gas, the procedures given for sample preparation also is valid for wash water and MEA solvent. Two complementary *extraction procedures based on liquid-liquid-extraction (LLE) and solid phase extraction (SPE)* are given as central parts of the procedure. *However, if one single common extraction method for both nitrosamines and nitramines is aimed, the LLE extraction procedure is recommended.* The sample preparation methodologies presented have a considerable potential for further optimization.

Mass spectrometric methodology has been developed that cover the list of analytes given in the scope. The methods are based on liquid chromatography with triplequadrupole mass spectrometry (LC-MS-MS-QQQ) for nitrosamines, nitramines, amines and aldehydes, and on gas chromatography with mass spectrometry (GC-MS) for the alkylamines and ammonia and on gas chromatography with nitrogen chemiluminescence (GC-MS-NCD) for total nitrosamine. The analytical methods have been adapted to the procedures for sampling (capture of analyte) and sample preparation (work-up). The instrumental methodologies presented may have potential for further optimization.

6 Recommendation for further work

Flue gas sampling of gases with high aerosol contents and compounds with widely varying properties is challenging. Classical sampling methods are not rigorously verified; this is obvious since the well-established standards for e.g. dioxin sampling is currently under revision, since considerable concern has been raised with respect to the appropriate collection of sub-micron particles/aerosols. The uncertainty is based on the simple fact that sampling systems are not verified rigorously in a closed system, were full control of the mass balance is established. For the time being, the verification of sampling systems is based on the following reasoning: Provided that in a sequence of collection stages, the next to final stage has a concentration of an analyte in question of less than 1 % based on the sum of analytes in all stages, the system is performing properly. Provided all gases are condensed in the absorption stages, this is correct. However, if sub-micron aerosols are present, these will not necessarily be captured in an impinger, especially if the sampling train is not operated at design conditions.

The presented comprehensive work on sampling shows that the collection of volatile compounds in an aqueous condensate phase is possible. The procedure generates a clean matrix for analysis of the compounds without impurities from absorption additives like sulphuric acid or sulfamic acid. However, the recent discussions on amount and type of aerosols with a droplet size of $d_p \leq$ 1 µm requires consideration. Even though we propose the extension of the system sampling system (primarily condenser based) with a micro filter, this system needs to be verified properly.

A SINTEF project is initiated to test the combination condenser and subsequent microfiltration with respect to applicability, performance and possible uncertainties related to accumulation of analytes in the filter media and operation of the system.

Overall method uncertainty needs confirmation and experimental verification.

7 Supplementary information

ANALYTICAL SENSITIVITY FOR THE COMBINED METHODOLGIES

FLUE GAS SAMPLES

Table 7-1 below shows the analytical sensitivity in flue gas condensate samples. The concentrations are derived by the following method:

a) Sensitivity of instrument verified on a liquid sample derived from flue gas
b) Extraction process to increase concentration of analytes in sample (primary removal of water). Data give the recovery of a liquid-liquid extraction (LLE) process for each individual compound. The volume of the sample is reduced by a factor of 100X, however the concentration change (given in % recovery) is lower compared to the volume change because of interfacial mass transfer effects.
c) The extraction process improves the sensitivity for a given compound with a factor of e.g.: 20 for NDELA, thus limit of quantitation (LOQ, S/N>10) in the untreated liquid is: 0.1 [μg/l] / 20 = 5 [ng/L]
d) Back calculation from the extracted liquid sample (column c) to flue gas concentration (liquid sample volume and flue gas volume) results in: (5 [ng/L] * 0,05 L) / 1Nm^3 = 0,25 [ng/L]

Table 7-1: Analytical sensitivity in flue gas condensate samples.

Analyte group	Analyte	Instrument LOQ in condensate extract (ug/L) a)	Extraction recovery for individual compounds [%] b)	LOQ in 100X concentrated condensate extract (ng/L) c)	LOQ in 100X concentrated condensate extract# (ng/Nm3) d)
Nitrosamines	NDMA	0.1	20 (LLE)	5	0.25
	NDEA	0.1	40 (LLE)	2.5	0.13
	NMOR	0.1	60 (LLE)	1.7	0.09
	NPIP	0.1	50 (LLE)	2	0.1
	NDELA	0.1	20 (LLE)	5	0.25
	NPZ	0.1*	0 (LLE/SPE)	100*	5
	DNPZ	2.5	20 (LLE)	125	6.25
Nitramines	MEA-nitramine	0.1	>90 (SPE) 5% (LLE)	25	1.25
	AMP-nitramine	0.1	>90 (SPE) 30 (LLE)	3	0.15
	PZ-nitramine	1*	0 (LLE/SPE)	1 000*	50
Solvent amines	MEA	0.6*	NA	600*	30
	DEA	1*	NA	1 000*	50
	PZ	0.4*	NA	400*	20
	AMP	0.4*	NA	400*	20
Alkylamines	Methylamine	1*	NA	1 000*	50
	Ethylamine	1*	NA	1 000*	50
	Dimethylamine	1*	NA	1 000*	50
	Diethylamine	1*	NA	1 000*	50
Aldehydes	Formaldehyde	10	NA	10 000*	500
	Acetaldehyde	10	NA	10 000*	500
	Ammonia	1 000	NA	1 000 000*	50 000

\# = Calculation based on an assumed condensate volume of 0.05L and a sampled flue gas volume of 1 Nm3 (corresponding to ca.1 hour sampling).
* = No extraction or concentrating applicable to condensate because of amine functionality.
Must be analyzed in condensate or concentrated condensate

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WASH WATER SAMPLES

Table 7-2 below shows the analytical sensitivity in wash water samples

Table 7-2: Analytical Sensitivity in wash water samples.

Analyte group	Analyte	INSTRUMENT LOQ IN WASH WATER EXTRACT (ug/L)	LOQ IN 100X CONC. WASH WATER EXTRACT (ng/L)
Nitrosamines	NDMA	0.1	5
	NDEA	0.1	0.13
	NMOR	0.1	0.09
	NPIP	0.1	2
	NDELA	0.1	5
	NPZ	0.1*	100*
	DNPZ	2.5	125
Nitramines	MEA-nitramine	0.1	25
	AMP-nitramine	0.1	3
	PZ-nitramine	1*	1 000*
Solvent amines	MEA	0.6*	600*
	DEA	1*	1 000*
	PZ	0.4*	400*
	AMP	0.4*	400*
Alkylamines	Methylamine	1*	1 000*
	Ethylamine	1*	1 000*
	Dimethylamine	1*	1 000*
	Diethylamine	1*	1 000*
Aldehydes	Formaldehyde	10*	10 000*
	Acetaldehyde	10*	10 000*
	Ammonia	1 000*	1 000 000*

* = No extraction or concentrating applicable. Must be analyzed in wash water.

SOLVENT AMINE SAMPLES

Table 7-3 below shows the analytical sensitivity in solvent amine (MEA) samples after removal of MEA.

Table 7-3: Analytical Sensitivity in Solvent Amine (MEA) samples.

Analyte group	Analyte	INSTRUMENT LOQ IN SOLVENT (MEA) EXTRACT (ug/L)	LOQ IN 10X CONC. SOLVENT (MEA) EXTRACT (ng/L)
Nitrosamines	NDMA	0.1	50
	NDEA	0.1	25
	NMOR	0.1	17
	NPIP	0.1	20
	NDELA	0.1	50
	NPZ	0.1*	100*
	DNPZ	2.5	125
Nitramines	MEA-nitramine	0.1	25
	AMP-nitramine	0.1	30
	PZ-nitramine	1*	1 000*
Solvent amines	MEA	0.6*	600*
	DEA	1*	1 000*
	PZ	0.4*	400*
	AMP	0.4*	400*
Alkylamines	Methylamine	1*	1 000*
	Ethylamine	1*	1 000*
	Dimethylamine	1*	1 000*
	Diethylamine	1*	1 000*
Aldehydes	Formaldehyde	10*	10 000*
	Acetaldehyde	10*	10 000*
	Ammonia	1 000*	1 000 000*

* = No extraction or concentrating applicable. Must be analyzed in amine solvent.

8   Abbreviations used in text or Appendices

NDMA	N-Nitrosodimethylamine
NDEA	N-Nitrosodiethylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosppiperidine
NDELA	N-Nitrosodiethanolamine
NPZ	N-Nitrosopiperazine
DNPZ	1,4-Dinitrosopiperazine
MEA	Monoethanolamine
DEA	Diethanolamine
PZ	Piperazine
AMP	2-Amino-2-methyl-1-propanol
DNPH	Dinitrophenylhydrazine
BSC	Benzenesulfonylchloride
HDPE	High Density Polyethylene

9 References

[1] Wittgens, B., A. Einbu, K. Zahlsen and E. Hunnes: H&E TQP ID1: Establish Sampling and Analytical Procedures for potential harmful components in post combustion amine based CO2-capture, Subtask 1: Design of Sampling Points in treated flue gas, FM07-AJZ00-RA-0001, SINTEF Report F16137, 2010

[2] Wittgens, B., A. Einbu, K. Zahlsen, A. Brunsvik, E. Hunnes and C Johansson: H&E TQP ID1: Establish Sampling and Analytical Procedures for potential harmful components in post combustion amine based CO2-capture, Subtask 2: Procedures for Manual Sampling, FM07-AJZ00-S-RA-0001-04, SINTEF Report F16586, 2010

[3] Wittgens, B., A. Einbu and K. Zahlsen: H&E TQP ID1: Establish Sampling and Analytical Procedures for potential harmful components in post combustion amine based CO2-capture, Subtask 3: Online Sampling and Analysis, , SINTEF Report F16785, 2010

[4] Zahlsen, K., K. Vernstad, T. Holten, A. Brunsvik, A. Einbu, B. Wittgens and P.O. Wiig: H&E TQP ID1: Establish Sampling and Analytical Procedures for potential harmful components in post combustion amine based CO2-capture, Subtask 5: Establish analytical procedures, FM07-AJZ00-S-RA-0003-03, SINTEF Report F18774, 2011

[5] Leithe, W.; Die Analyse der Luft und ihrer Verunreingungen, Wissenschaftliche Verlagsgesellschaft mbH, Stuttgart, 1968

[6] VDI 2452-Part1, Air Pollution Measurement; measurement of total fluoride ion concentration; Impinger method, 1978

[7] Hinds, W.C..; Aerosol Technology Properties, Behavior and Measurements of airborne particles, Wiley, 1999

[8] EN 13284-1: Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method.

[9] VDI 2066-2: Measurement of particulate matter; manual dust measurement in flowing gases; gravimetric determination of dust load; tubular filter devices.

[10] VDI 3868 Part 1: Determination of total emissions of metals, metalloids and their compounds – Manual measurement in flowing, emitted gases- Sampling system for particulate and filter passing matter, 1994.

[11] Environnemt S.A.; http://www.environnement-sa.com

[12] Rintenko: Gassnova Kårstø Amine Emission and Monitoring, WTO nr 24- Open version, Nr. RF0041U-100A-001, 2010

[13] Personal communication with Peter Zemek, MIDAC Cooperation

[14] VDI 3496, Part 1 Measurement of gaseous emissions – Measurement of ammonia concentration, 1982

[15] Personal Communication, Jürgen Reinmann, Environnement, Germany

[16] Zahlsen, K., A. Brunsvik, A. Einbu, and B. Wittgens: H&E TQP ID1: Establish Sampling and Analytical Procedures for potential harmful components in post combustion amine based CO2-capture, Subtask 4: Literature Study, SINTEF Report F16585, 2010